THE ION EXCHANGE AND SORPTION PROPERTIES OF MICROCRYSTALS OF INORGANIC OXIDES

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by

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SUMMARY

Detailed studies have been made on the ion exchange and sorptive properties of aqueous dispersions of single crystals of beta-iron oxide hydroxide and monoclinic zirconia. These microcrystals were prepared in the laboratory and characterised by transmission electron micrographs and electron diffraction patterns. The crystals are typically 1000-2000 Å in size and have amphoteric ion exchange properties. In this work, a multi-ion selective electrode titration system working with a highly developed computational and graphic system was developed to determine the ion exchange and sorption properties of these crystals. Ion sieving characteristics of βFeOOH have been proven and extended to include a separation of chloride from solutions containing iodide and bromide and, in alkali, exclusion of sodium ion. Fluoride uptake is determined by ion selective electrode response and alkaline earth uptake is determined by flame emission spectroscopy.

Single ion exchange uptake of anions in acid and cations in base is explained by a Donnan model. This predicts anion (cation) capacity to be a single-valued function of the negative logarithm of the corresponding acid (base) activity in the equilibrium solution. Adsorptive properties of fluoride ion on monoclinic zirconia is explained by ligand exchange or incorporation of this adsorbate into the framework of the oxide. Exchange is shown to be reversible for most simple univalent ions and variations in exchange capacity controlled by solution pH and salt concentrations.

CHAPTER 1

INTRODUCTION

INTRODUCTION

Ion exchange is the reversible exchange of ions of the same charge sign between a solution, usually aqueous, and an insoluble solid in contact with it. The subject was rediscovered (from biblical times) more than a century ago with the realisation of "base exchange" properties of soils by Thompson (1) and Way (2), later found to be mainly due to clay content. Many years were to elapse before the mechanism of exchange was understood yet ion exchange capacity was recognized as a very important factor in soil fertility. Along with clay content, soil fertility is further contributed by the humic acid component, the residue of decayed organic matter, rich in hydroxyl and carboxyl exchange groups.

Sometimes exchange occurs at the surface, as in some clays, but more commonly the exchanger has a porous structure that may be crystalline, with cavities, channels, or layered spaces that let ions move in and out. Various natural minerals, particularly the zeolitic group of aluminosilicates were shown by Lemberg to have ion exchange behaviour (3,4). This discovery lead to their application to water softening (5,6). Another important property of zeolites is their 'molecular sieve' action: some molecules are readily taken up by the zeolitic framework, while others are excluded because their size does not allow them to enter the pore. This property was studied extensively by Barrer (7). Specific separations of ions can be carried out by the ion sieving behaviour of certain zeolites. This property has been exploited in the treatment of radioactive waste solutions, for example by the use of

clinoptilolite which selectively removes trace caesium ion from solutions containing much higher concentrations of sodium and other ions (8).

Synthetic aluminosilicates may be divided into three main groups : amorphous, two dimensional layered aluminosilicates (synthetic analogues of clay minerals), and aluminosilicates with rigid, three dimensional structures (zeolites). A great deal of work has been carried out on investigating the positions of various cations and water within the framework of zeolites (9) which is important for understanding the ion exchange and ion sieving properties of these materials. The imbibement of salt molecules in zeolites obeys the Donnan distribution law (10). This trend toward providing a more exact explanation of ion exchange reactions rather than studying purely practical separation application is helpful in the understanding of the ion exchange mechanisms applied to the materials used in this work.

However, the zeolites have some practical disadvantages. They can be unstable in acids and alkali and often have extremely low diffusion coefficients making the exchange process very slow and impractical in large scale applications.

A great step forward toward general use of ion exchange processes was made in 1935 when synthetic organic ion exchange resins were introduced as practical exchangers by Adams and Holmes (11). The first synthetics were polymeric condensations of formaldehyde with suitable phenols or arylamines. In these resins the aromatic rings

carried ionic functional groups. Improved resins were introduced by D´Alelio (12) based on the copolymerization of styrene with the crosslinking agent, divinyl benzene. This can be sulphonated to produce a cation exchanger or chloromethylated and treated with a tertiary amine to give an anion exchanger. Nearly all current industrial and large scale laboratory applications of ion exchange are based on such resins. Following the synthesis of organic resins it was possible to vary the properties of ion exchangers in a systematic manner. This greater flexibility allowed resins to be synthesised for specific applications.

The organic resins, however, suffer from two major disadvantages: they are thermally unstable and cannot be used at temperatures above 150° C for sulphonic acid resins and not above about 50° C for quaternary ammonium resins. They also tend to breakdown in the presence of large doses of ionizing radiation.

For these reasons, a need arose to study the inorganic class of ion exchangers. In general, the inorganics are much more selective for certain ions and more cheaply prepared than their organic counterparts. Aluminosilicates are often confined to specific purposes and the process of surveying the properties of other inorganic types arose.

The synthetic inorganic ion exchange materials may be divided into the following main groups :

1. Aluminosilicates
2. Salts of heteropolyacids
3. Insoluble ferrocyanides
4. Acidic salts of multivalent metals

5. Hydrous oxides

The excellent book by Amphlett (13) has covered this field up to 1965. The thorough review by Veselý and Pekárek (14) covers 1965-1970 and another article by De and Sen (15) review the work done during 1970-1976.

The basic physiochemical and ion exchange properties of salts of heteropolyacids have been widely surveyed in the book by Amphlett (13). Recent applications include separation of rubidium, caesium, potassium, tellurium, and silver (16).

Ferrocyanide ion exchangers act as cation exchangers with a high affinity for heavy alkali metal ions, especially for caesium. It is assumed (17) that the property which is responsible for the affinity of various ferrocyanides towards alkali metal ions is the intensity of the electrostatic field on the surface of the cation in the ferrocyanide. The lower the value of this intensity, the higher the affinity for alkali metal ions. Ferrocyanide resins have been prepared by treatment of strongly basic anion exchange organic resins with metal salt and $K_4Fe(CN)_6$ solutions. Removal of caesium from radioactive effluent and separation of caesium from barium for the purpose of barium preparation (18) have been described.

A wide range of insoluble acidic salts of multivalent metals have been descibed as ion exchangers. Among the metals studied have been zirconium, thorium, titanium, cerium (IV), tin (IV), aluminium, iron (III), chromium (III), uranium (VI), and the anions employed include phosphate, arsenate, antimonate, vanadate, molybdate,

tungstate and silicate. Most of the early materials studied were amorphous gels. Recent developments in the study of these materials have led to successful preparations of well-defined crystalline compounds. Zirconium phosphate is the most notable example. It has a layered structure and exhibits ion sieve properties (19). Knowledge of the crystal structure is fundamental for a deeper understanding of the ion exchange process and its reversibility (20) as well as a solid basis for the interpretation of thermodynamic measurements (21). It also defines a limited number of well-defined crystalline sites for exchange, as zeolites do, and hence new crystalline inorganic exchangers would be expected to have much improved selectivity patterns, compared with the less well-defined amorphous analogues.

The adsorptive properties of hydrous oxides, such as, alumina, silica and ferric oxide have been known for many years and it has been established that the mechanism for adsorption of simple ions is by ion exchange. The insoluble hydrous oxides form a large class and their properties have been studied extensively by authors such as Kraus, et al (22): $BeO.nH_2O$ (23), $Bi_2O_3.nH_2O$ (22,24), $MgO.nH_2O$ (23,25), $Al_2O_3.nH_2O$ (26), $Fe_2O_3.nH_2O$ (27,28), $TiO_2.nH_2O$ (29,30), $SiO_2.nH_2O$ (31), $ZrO_2.nH_2O$ (22,29,32), $ThO_2.nH_2O$ (29,33), $CeO_2.nH_2O$ (34), $Cr_2O_3.nH_2O$ (22), $La_2O_3.nH_2O$ (23), $SnO_2.nH_2O$ (35), $WO_3.nH_2O$ (29),$MoO_3.nH_2O$ (22), $Sb_2O_5.nH_2O$ (36), $MnO_2.nH_2O$ (37). Hydrous oxides are of particular interest for theoretical and practical purposes

because most of them can function as both anion and cation exchangers. That is, they exhibit amphoteric behaviour, exchanging anions in acidic and cations in alkaline solutions. Although, their progress has been extended to include study of the sorption properties of mixed hydrous oxide systems which enable changes to be made to their classically amphoteric nature. By proper choice of metal ions, it is possible to prepare a mixed oxide having anion sorption properties in neutral and alkaline media (38). Also, mixed hydrous oxides have interesting applications in the field of solid state proton conductors for fuel cells, for example, $[Zr_2Cr(OH)_6]OH.nH_2O$ (39). One of the most attractive features of hydrous oxide adsorbants, compared with standard organic ion exchange resins, is their unusual and sometimes unique selectivity.

pH titration curves are used frequently to characterise the functional groups of the ion exchangers. This method is particularly useful for oxide materials due to their amphoteric nature. For example, zirconia (29) and thoria (29) show monofunctionality while hydrated alumina oxide (26) indicates that this material is a monofunctional cation exchanger, but a trifunctional anion exchanger. From the pH titration curves of most hydrous oxides it is clear that they are weak acid or weak base exchangers. The mechanisms of exchange are discussed in Chapter 2.

The hydrous oxide group of exchangers have been studied in this laboratory and the continuation of this work is the subject of this thesis. Paterson and Fryer with their coworkers Hutchison, Gildawie, and Rahman (40,41,42,43,44) have prepared a wide range of crystalline

oxide hydroxides. Transmission electron microscopy was used for characterisation of these materials and pH titration methods were advanced. The basic methodology for titrations was laid out and a consistent theoretical interpretation of the ion exchange mechanism was obtained.

In this thesis research, titration methods were improved and expanded to include direct, continuous monitoring of most, if not all the ions involved in exchange or sorption on the crystals with ion selective electrodes. Electrodes provide great flexibility and reasonable speed to study a number of equilibrium states. Electron microscopy was also used to confirm the crystalline state of, in particular, beta-iron oxide hydroxide and monoclinic zirconia exchangers in various ionic forms and after exchange titrations. In parallel to this, computer methods of general applicability have been developed to interpret titration data and to yield ion exchange capacities for oxide hydroxides.

Previous studies confirmed the exclusion of perchlorate (43) from the pore structure of βFeOOH. In this thesis, the exclusion of iodide and bromide further augmented the anion sieve characteristics of these crystals. Fluoride was shown to be taken up on βFeOOH and zirconia. The expectation of surface Donnan equilibrium exchange and protonation mechanism would be challenged by the more complex uptake of fluoride.

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CHAPTER 2

ION EXCHANGE AND SORPTION PROCESSES

2.1 Surface Structure of Oxides and Donnan Equilibrium

Insoluble hydrous oxides form a large class of synthetic inorganic ion exchangers and adsorbants. The hydrous oxides are of particular importance because of the high concentration of variable fixed charge on their matrices. Ion exchange, in contrast to sorption, is a stoichiometric process. Electroneutrality is preserved by mobile counterions (of opposite charge to the fixed charges) which move in from the external solution close to the fixed charge that is bound to the insoluble microporous solid oxide.

The surface structure of an oxide in the presence of water is different from its bulk crystal structure due to surface hydration. The resulting oxide surface is covered with a layer of hydroxyl groups, which directly determine most of its surface chemistry. In acid media, hydrogen ions are considered to react with the attached hydroxide ions of the solid to yield water molecules which remain attached to the metal. The system acquires a positive charge. Electroneutrality is preserved by the anions of the acid becoming included in the solid as readily diffusible counterions, i.e. the oxide has become an anion exchanger. This is illustrated for βFeOOH in Eq. [2.1] or Eq. [2.2] and other oxyhydroxides are considered to behave similarly. Barred species represent pore sites in the exchange.

$$\overline{\text{FeOOH}} + \text{H}^+_{aq} + \text{Cl}^-_{aq} = \overline{\text{FeOOH}_2^+\text{Cl}^-} \qquad \text{Eq. [2.1]}$$

$$\overline{\text{FeOOH}} + \text{H}^+_{aq} + \text{Cl}^-_{aq} = \overline{\text{FeOCl}} + \text{H}_2\text{O} \qquad \text{Eq. [2.2]}$$

Similarly, in alkaline media, hydroxylation of the oxide surface creates negative charges and the cation counterions become incorporated in the solid retaining a high degree of diffusibility. Two possible mechanisms are shown, Eq.s [2.3] and [2.4].

$$\overline{FeOOH} + Na^+_{aq} + OH^-_{aq} = \overline{FeO(OH)_2^-Na^+} \qquad \text{Eq. [2.3]}$$

$$\overline{FeOOH} + Na^+_{aq} + OH^-_{aq} = \overline{FeO^-Na^+} + H_2O \qquad \text{Eq. [2.4]}$$

When an exchanger is placed in water, ions would diffuse into the surrounding solution and this high concentration of electrolyte in the solution would drive water into the exchanger. If the ions carried no electric charge, these concentration differences would be levelled out by diffusion. Ions, however, carry charge and so the first few ions which diffuse build up an electric potential between the two phases: the Donnan potential (1). This electrical potential is a consequence of the uneven distribution of diffusible ions between two phases at equilibrium. The Donnan potential always acts to attract counterions (back) into the charged matrix or pore structure and to repel coions. In dilute solutions therefore, an ion exchanger absorbs water, but relatively little salt. The coion (the excluded ion of same sign as the fixed charge) is hindered by the presence of the nondiffusible fixed charge. Therefore, the presence of Donnan potential at the exchanger solution interface automatically favours counterion exchange and coion exclusion.

2.2 Adsorption Surface Charge and Protonation of Hydroxide Groups

The potential built up at the solution/exchanger interface is generated by an electrical double layer. The electric charge on the surface is balanced by a region of opposite charge in the solution adjacent to the solid interface. Bowden, et al. (2) have examined the electrical double layer theory. In their generalised model for adsorption on an oxide surface, the solid/solution interface is conveniently divided into three regions:

1. the potential determining ions (hydrogen and hydroxyl ions)
2. the specifically adsorbed ions (discussed below)
3. the diffuse layer of counterions and coions

A site binding model, combining the theory of Bowden, et al. with the specific coordinative interactions of solutes with the oxide surface, of amorphous iron oxyhydroxide is applied to the adsorption of metal ions by Davis and Leckie (3). Adsorption, unlike ion exchange, is not necessarily stoichiometric and there are studies underway that suggest a probable ligand exchange or incorporation of the adsorbate into the framework of the oxide (3,4).

The surface charge of the hydrous oxide is one of the factors determining the amount of adsorption. In aqueous solutions, the surfaces of hydrous oxides are made up of hydroxyl groups capable of showing weak acid behaviour and the extent to which they are protonated or dehydroxylated determines the surface charge (5). Analysis of pH electrode titrations cannot distinguish between protonation

of a hydroxyl group on the oxide matrix to form a coordinated water, Eq. [2.1], and the anion of the acid substituting a hydroxyl on the surface in the formation of a complex, Eq. [2.2]. We, therefore, have no hard evidence to suggest that the mechanism of exchange occurs by the formation of a charged hydrated group, Eq. [2.1], and therefore the extent of protonation determining the surface charge. Yet, this could be explained by the high surface charge densities of oxides. Stumm, et al. (6) suggest strongly structured, hydrogen bonded and chemisorbed water layer adjacent to the oxide surface give rise to higher surface charge densities than classical surfaces. This argument suggests a protonation of the uncharged surface sites in acid and correspondingly a deprotonation of uncharged surface sites in alkali.

2.3 The Pore Model for Capacity

A pore model for capacity was developed previously (7) to interpret pH titration experiments on oxide hydroxides. The discussion which follows refers specifically to the anionic exchange mechanism for βFeOOH, but other oxyhydroxides are thought to behave similarly. Analogous explanations to account for cationic capacity of these oxide hydroxides in base will be discussed later (see Section 7.2).

βFeOOH has been shown to have large ion exchange capacity for chloride in acidic solutions (7,8). This observation has been upheld by ion selective electrode

determinations in this work. The explanation for the major influence of chloride on capacity lies in the fundamental mechanism for exchange. Anionic uptake involves a thermodynamic coupling between the protonation reaction, by which positive charges are created in the matrix of the crystal and uptake of chloride (or other anion) occurs to compensate these charges. The term 'protonation' is not precisely defined, since the actual interaction between proton and βFeOOH is not known (see Section 2.2). Since the experimental evidence is a pH shift seen when the chloride ion is taken up by the exchanger, the effect could be one of protonation, dehydroxylation of pore sites or direct anion exchange with a hydroxyl group in the crystal structure. For thermodynamics it is only necessary to know that such an interaction exists.

$$\overline{\text{FeOOH}} + \overline{H^+} = \overline{\text{FeOOH}_2^+} \qquad \text{Eq.[2.5]}$$

Bars over species indicate that the reactions are assumed to occur within the hollandite pores of βFeOOH in this model. Eq.[2.5] is the base protonation reaction for which an acid dissociation constant, K_a, may be defined:

$$K_a = \bar{a}_{\text{FeOOH}} * \bar{a}_{H^+} \; / \; \bar{a}_{\text{FeOOH}^{2+}} \qquad \text{Eq.[2.6]}$$

The protons of Eq.[2.5] are pore protons which are in Donnan equilibrium (see Section 2.1) with those in the external solution:

$$\overline{H^+} = H^+_{aq} \qquad \text{Eq.[2.7]}$$

Because this is an interfacial equilibrium involving charge separation, and driven by the affinity of the protonation reaction, the activities of the proton in each phase are not equal, but depend upon the Donnan potential $(\bar{\psi}-\psi)$:

$$\bar{a}_{H+}/a_{H+} = \exp\ (-F(\bar{\psi}-\psi)/RT) \qquad \text{Eq.[2.8]}$$

If only the equilibria of Eq.'s [2.5] and [2.7] applied then the protonation would not proceed because uncompensated transfer of positive charge from solution to pore would create an enormous positive Donnan potential. There would be no protonation of pore sites regardless of the favourability of $\bar{K}_a$ [Eq.2.6] to protonation.

The process can only occur if chloride, or other counterion, may enter the pores. This allows effective electroneutrality to be preserved, while large numbers of protons, now accompanied by chloride, are transferred. The Donnan equilibrium relationship for electrolyte uptake of acid is achieved:

$$\bar{a}_H * \bar{a}_{Cl} = a_H * a_{Cl} \qquad \text{Eq.[2.9]}$$

Since, by definition, $\bar{K}_a$ is constant, the activities of the pore species, $\overline{FeOOH}$, $\underline{Cl}$ and $\overline{FeOOH_2}^+$, will be determined solely by the activity of the acid in solution:

$$\overline{\overline{FeOOH}} + H^+_{aq} + Cl^-_{aq} = \overline{\overline{FeOOH_2^+}} + \overline{Cl^-} \qquad \text{Eq.[2.10]}$$

$$K_a = (a_{\overline{\overline{FeOOH}}} * (a_H * a_{Cl}))/a_{\overline{\overline{FeOOH2+}}} * a_{\overline{Cl}} \qquad \text{Eq.[2.11]}$$

Under such conditions, a particular value of the activity of the external acid, $a_H * a_{Cl}$, or in logarithmic form, pA = pH + pCl, would define a unique pore condition and hence a unique pore capacity. The experimental chloride capacity would be a single-valued function of pA.

Plots of chloride capacity against pA for the titration data of Tables 6.1 and 6.2 are given in Fig. 6.3. The results show conclusively that chloride capacity of βFeOOH is a single-valued function of the activity of the total acid, pA, as predicted by the pore model above.

If in the general case an anion exchanger has such a pA dependency, where now pA = pH + pX, and X is an exchangeable anion, then it is clear that the anion, X, has an effect on an exchangers total capacity that is just as important as the pH effect.

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CHAPTER 3

PREPARATION AND CHARACTERISATION OF OXIDE HYDROXIDES

Introduction

Hydrous oxides are amorphous often gel-like inorganic oxide materials with ion exchange properties. In the past, detailed physical characterisation was often difficult as these materials were amorphous or poorly crystalline and, therefore, difficult to reproduce from batch to batch. In this laboratory reproducible crystalline analogues to the amorphous gels, called oxide hydroxides or oxyhydroxides, have been prepared which enable the study of their selectivities and ion sieve behaviour related to the crystal structure. The two crystalline forms studied here are βFeOOH and monoclinic zirconia.

Oxide hydroxides are prepared by hydrolysis of metal salt solutions under strict conditions. The hydrolysis of metal ions is the result of deprotonation of coordinated water molecules. When water molecules are bound to a metal ion, the formation of a metal oxygen bond weakens the oxygen hydrogen bond of the coordinated water molecule so that they are stronger acids than free water molecules. The greater the strength of the metal oxygen bond, which depends upon the size and charge of the metal ion, the greater the extent of hydrolysis.

An oxyhydroxide of a trivalent metal, M, has the composition MOOH and is intermediate between the oxide M_2O_3 and the hydroxide $M(OH)_3$. They were first thought to be hydrated oxides but later Kolthoff and Moskovitz (1) proved that they were oxide hydroxides.

The precipitation of oxyhydroxides from metal salt solutions is more complex than most precipitation processes

because nucleation and growth cannot solely be described by the deposition of ionic units upon a growing crystal nucleus. In this case, chemical reactions, olation and oxolation occur to form polynuclear species. (Olation is the formation of a hydroxyl bridge with the elimination of water. Oxolation is the formation of an oxo bridge at the expense of a hydroxyl bridge.) Both processes produce H^+ or H_3O^+ ions, causing a decrease in the pH of the solution.

$$(H_2O)_5\text{-}M\text{-}OH_2 \; H_2O\text{-}M\text{-}(OH_2)_5 \xrightarrow{\text{olation}} (H_2O)_5M\text{-}OH\text{-}M(OH_2)_5 + H_2O + H^+$$

$$(H_2O)_5M\text{-}OH\text{-}M(OH_2)_5 \xrightarrow{\text{oxolation}} (H_2O)_5M\text{-}O\text{-}M(OH_2)_5 + H^+$$

The final precipitated oxyhydroxide is based on either a chain-like or sheet-like structure.

Attempts have been made to substantiate these mechanisms and electron microscopic observation of partially hydrolysed metal salt systems, by Fryer, Paterson and Hutchison, have shown sheet and layer structures in agreement with the mechanism discussed (2). Such observations are not considered conclusive evidence since electron microscopic studies are made in the dry state under high vacuum and cannot always be related to solution structures.

3.1 Preparation of βFeOOH

3.1.1 Preparation of βFeOOH in the Chloride Form

βFeOOH microcrystals were prepared by the method of Matijević and Scheiner (3). Three liters of a stock solution 0.09 molar in ferric chloride and 0.01 molar in hydrochloric acid was prepared. This solution was passed through a 0.45 μm Millipore filter to remove any colloidal contaminants which might be present before hydrolysis was begun. The solution was poured into a three-necked, round-bottomed flask, which was fitted with a water condenser and a platinum resistance thermometer. The ferric solution was thermostated by a Haake TB32 programmable thermoregulator attached to the thermometer. Hydrolysis was performed at 90 ± 0.1 °C and the solution was magnetically stirred using a Teflon coated stir bar. After 24 hours the solution was cooled to room temperature and centrifuged. The precipitated crystals were redispersed in water acidified with hydrochloric acid to give the same pH as the mother liquor. This prevented possible precipitation of any partly hydrolysed iron. The washed dispersion was centrifuged once more. This procedure was repeated several times to wash the crystals until no precipitate of iron hydroxide could be obtained in the washings. The final dispersions were made with distilled water. They remained acidic due to the slow release of hydrochloric acid adsorbed during hydrolysis. The microcrystalline precipitate was then air dried overnight at 42 °C and stored in sealed glass bottles until required.

3.1.2 Preparation of βFeOOH in the Fluoride Form

In this thesis, chloride and fluoride exchange equilibria on βFeOOH have been studied using ion selective electrodes. It is documented that βFeOOH becomes unstable if less than 2% chloride (4) ion is present within its hollandite pore structure. The fluoride electrode results (see Section 6.2.4) suggested an attempt to prepare βFeOOH directly in the fluoride form was necessary.

The first attempt to prepare βFeOOH in the fluoride form was based on the method of Ohyabu and Ujihira (5). Crystals were precipitated as the hydrolysis product of a solution 0.1 molar in ferric nitrate heated at 70° C for 3 hours. Sodium fluoride was added to the solution to adjust the fluoride concentration to 0.1 molar. The precipitate was washed with distilled water and centrifuged 4 times. Then air dried at 62 °C for 24 hours. X-ray diffraction patterns showed the batch to be a mixture of geothite (αFeOOH) and magnetite (Fe_3O_4). This method was, therefore, unsuitable.

The second attempt to prepare βFeOOH in the fluoride form followed the method of Childs, Goodman, Paterson, and Woodhams (6). The crystals were prepared by hydrolysis of a solution 0.1 molar in ferric nitrate to which sodium fluoride was added before hydrolysis to give a F/Fe ratio of 1.0. Hydrolysis was carried out at 70° C for 7 days. The dispersion was then dialysed against distilled water. The sample was dried at 50 °C and lightly ground. Electron diffraction patterns showed these crystals to be pure βFeOOH (Section 3.3.1).

3.2 Preparation of Monoclinic Zirconia

Monoclinic crystals of zirconia were prepared by the method of Clearfield (7) incorporating improvements made by Paterson and Rahman (8). A solution 1 molar in zirconium was prepared by dissolving zirconyl chloride in distilled water yeilding a pH of about 0.4. The solution was passed through a Millipore filter and its pH adjusted to 2.5 by the addition of 0.5 molar ammonium hydroxide with rigorous stirring to prevent precipitation of amorphous zirconia. The solution was then transferred into a three-necked, round-bottomed flask and refluxed at 100 °C for 24 hours. A milky white precipitate was formed. The mixture was separated by centrifuging. The supernatant was again adjusted to pH 2.5 using ammonium hydroxide and refluxed at 100 °C for 24 hours. Periodically small samples of solution were removed and tested for unhydrolysed zirconium, by base addition, and as soon as it was absent the reflux was discontinued. The crystals were then redispersed, filtered and washed with distilled water, centrifuged and air dried at 56 °C and stored in a glass sealed bottle for further use.

3.3 Characterisation of Oxide Hydroxides

3.3.1 βFeOOH

Samples of βFeOOH, prepared as described in Sections 3.1.1 and 3.1.2, were examined by high resolution transmission electron microscopy. The code used for the various samples was as follows:

βFeOOH(90) represents the standard batch of ion exchanger used in most of this work prepared by the method of Matijević and Schiener hydrolysed at 90 °C (3). βFeOOH(A) represents the ion exchanger obtained by the method of Childs, Goodman, Paterson and Woodhams (6). βFeOOH(F) represents a sample of βFeOOH(90) equilibrated with sodium fluoride at pH 5 and then washed clear of sodium ion. βFeOOH(Ba) represents a sample of βFeOOH equilibrated with barium and similarly washed.

Electron micrographs of samples βFeOOH(90) longitudinal, βFeOOH(90) cross-sectional, βFeOOH(A), βFeOOH(F) and βFeOOH(Ba) are given in Plates 1 to 5, respectively. In all cases the micrographs showed typical cigar-shaped particles. Plate 2 fortunately captured the square cross-sectional view. Electron diffraction patterns of βFeOOH(90), βFeOOH(A) and βFeOOH(F) are shown in Plates 6 to 8, respectively. The single crystal diffraction d-spacings obtained from these Plates were identified as βFeOOH by comparing the measured d-spacings with the standard A.S.T.M. values for βFeOOH as shown in Table 3.1. Typically, the crystals were some 2000 x 400 x 400 $Å^3$ with no significant variation according to the method of preparation.

3.3.2 Monoclinic Zirconia

Monoclinic zirconia prepared by the method of Clearfield (7) as described in Section 3.2 was examined by high resolution transmission electron microscopy.

ZrO_2 represents the batch prepared by the method of Clearfield. ZrO_2(F) represents a sample equilibrated with sodium fluoride. Electron micrographs for these two samples are given in Plates 9 and 10. The X-ray diffraction pattern for ZrO_2 is given in Plate 11.

The crystalline d-spacings measured from Plate 11 are recorded in Table 3.2. Comparison of the measured spacings with A.S.T.M. values established the identity of particles as monoclinic zirconia. Only one diffraction pattern is obtained from the sample and so it was concluded that only one crystalline form of zirconia was present (2). The observed 'star' and 'pod' shapes of the crystals was due to observation of the monoclinic crystal, flat on the grid surface, star-shaped, and 90° to the grid plane, pod-shaped. 'Star' shaped crystals are predominant in the more stable position.

Table 3.1 Crystalline d-spacings for βFeOOH prepared in this study

βFeOOH(90)	βFeOOH(A)	βFeOOH(F)	βFeOOH A.S.T.M. 13-157
d(Å)	d(Å)	d(Å)	d(Å)
7.26	7.30	7.33	7.40
5.11	5.22	5.19	5.25
3.70	3.63	-	3.70
3.27	3.31	3.31	3.31
-	2.59	2.58	2.62
2.56	-	-	2.54
2.44	-	-	2.34
-	2.28	2.28	2.29
-	-	-	2.10
-	-	-	2.06
-	-	1.94	1.94
-	-	-	1.75
1.61	-	1.64	1.64
-	1.53	-	1.52
-	1.50	1.50	1.50
1.41	-	-	1.44

Table 3.2 Crystalline d-spacings of monoclinic zirconia prepared in this study

Measured values d(Å)	A.S.T.M. values d(Å)
5.11	5.04
3.72	3.69
-	3.16
-	2.83
-	2.62
2.54	2.54
2.22	2.21
-	2.18
2.03	2.01
1.83	1.84
-	1.82
-	1.69
1.67	1.66

PLATE 1

PLATE 1

Electron Micrograph of βFeOOH(90) longitudinal view

Prepared by the method of Matijević and Schiener (3)

PLATE 2

PLATE 2

Electron Micrograph of βFeOOH(90) cross-sectional view

Prepared by the method of Matijević and Schiener (3)

PLATE 3

PLATE 3

Electron Micrograph of βFeOOH(A). Prepared by the method of Childs, Goodman, Paterson and Woodhams (6)

PLATE 4

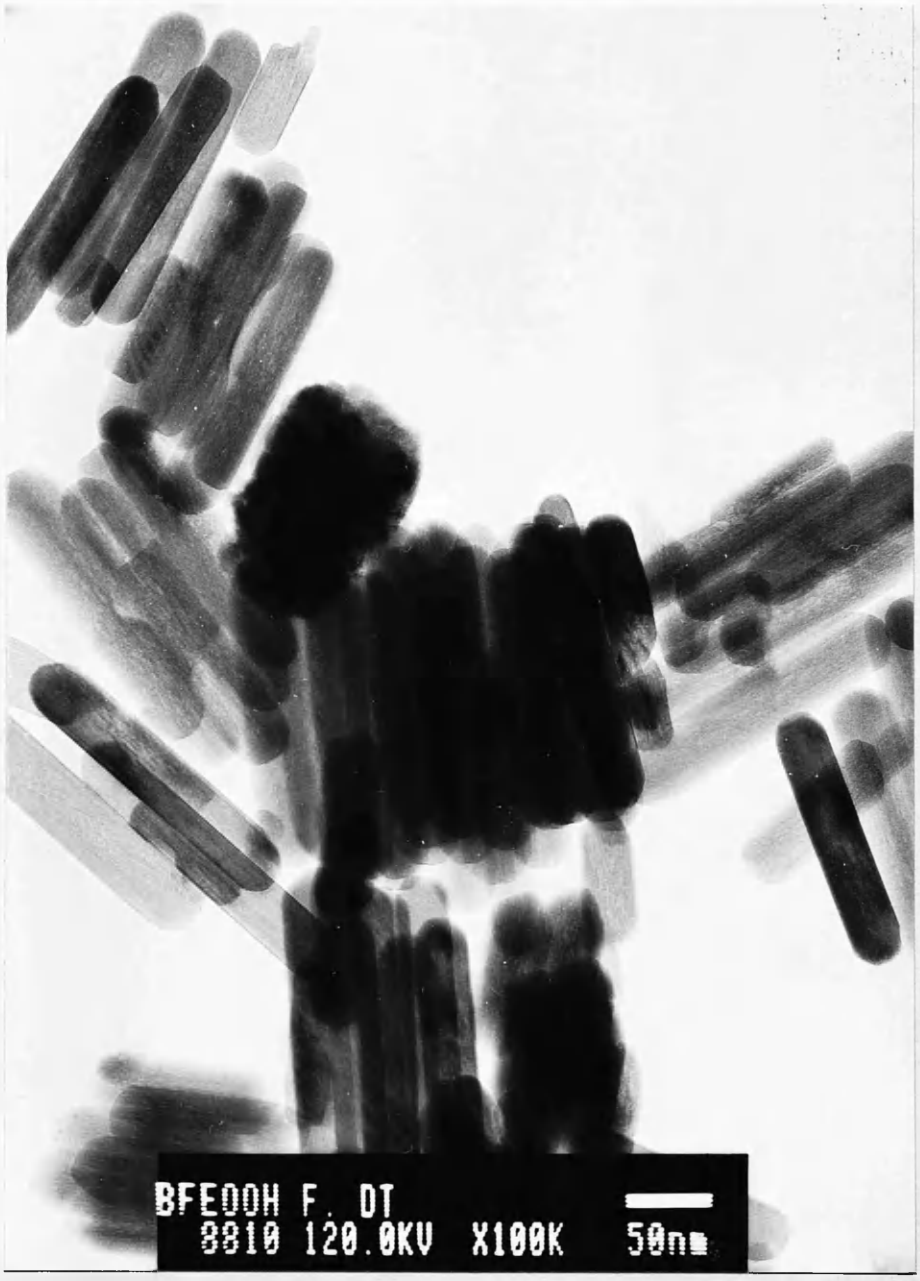

PLATE 4

Electron Micrograph of βFeOOH(F). A sample of βFeOOH(90) equilibrated with sodium fluoride

PLATE 5

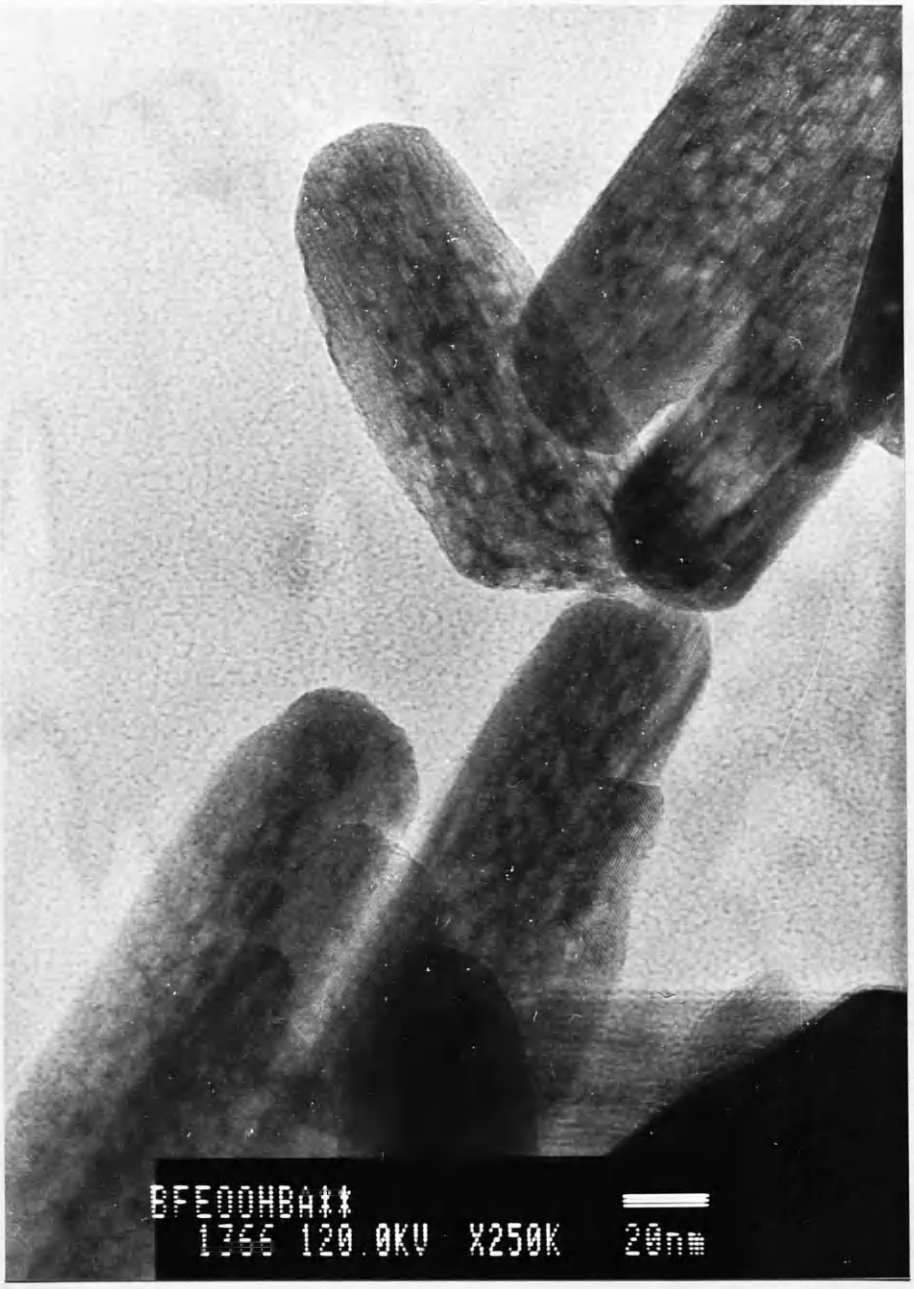

PLATE 5

Electron Micrograph of βFeOOH(Ba). A sample of βFeOOH(90) equilibrated with barium chloride

PLATE 6

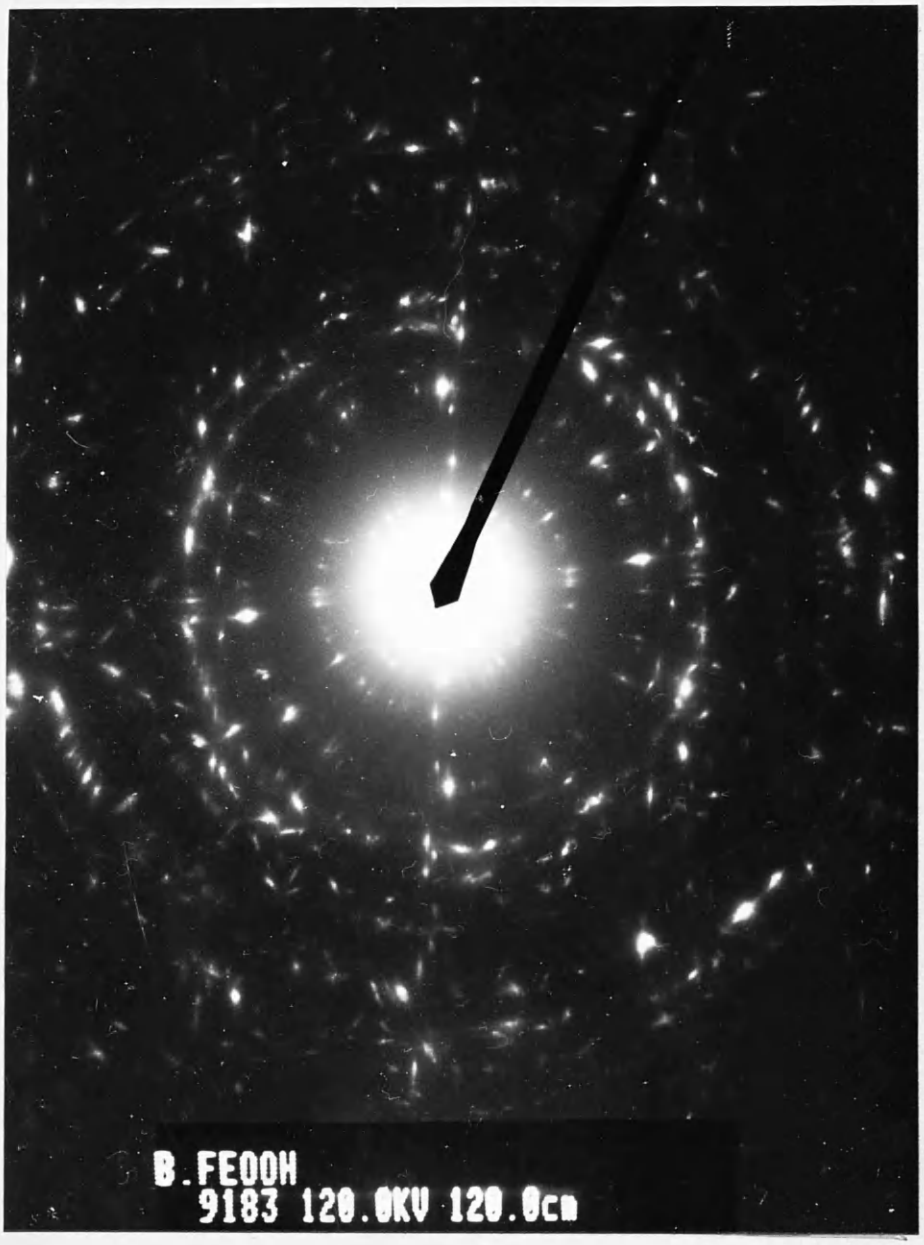

PLATE 6

Electron Diffraction Pattern of βFeOOH(90)

d-spacings given in Table 3.1

PLATE 7

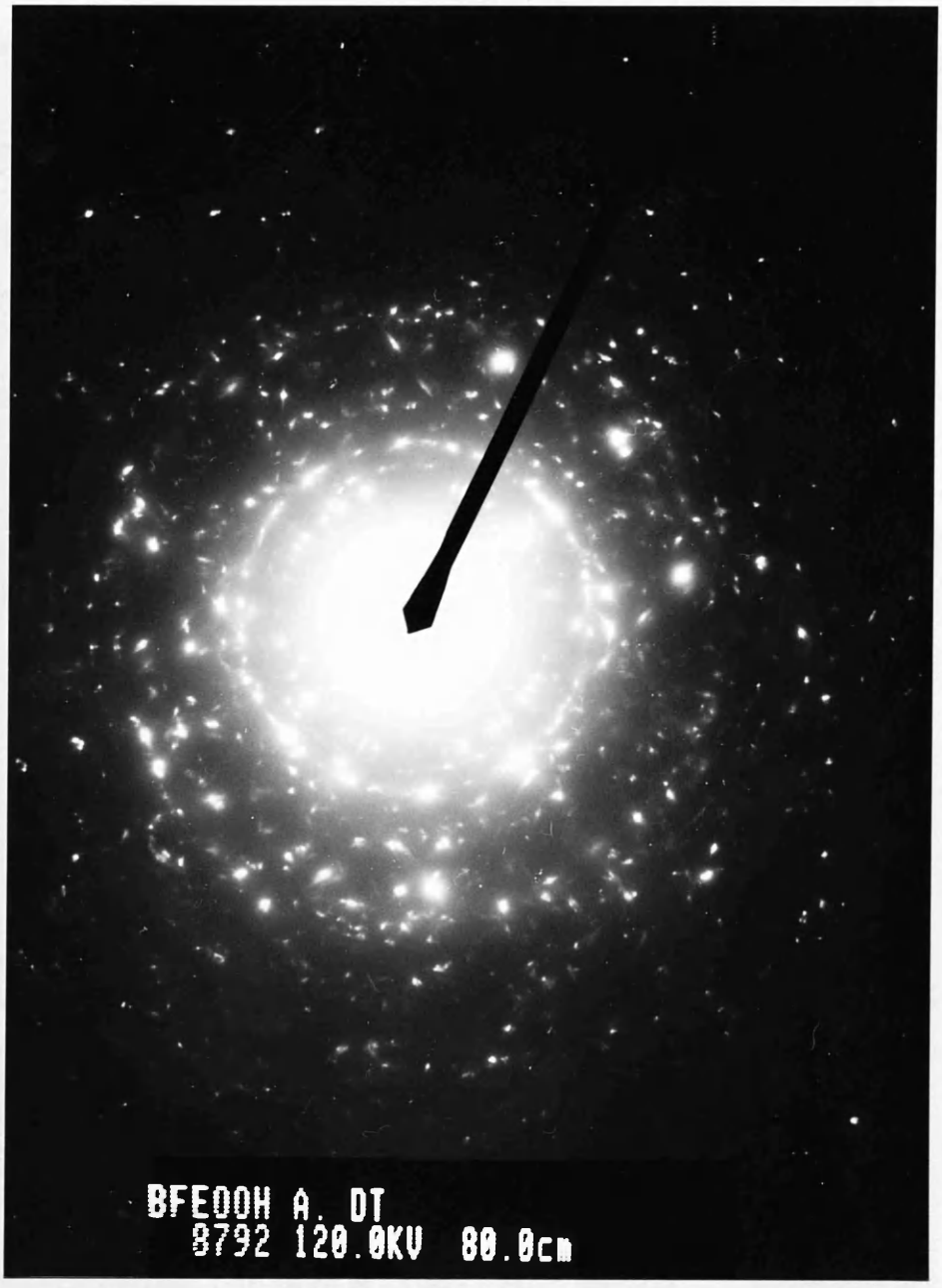

PLATE 7

Electron Diffraction Pattern of βFeOOH(A)

d-spacings given in Table 3.1

PLATE 8

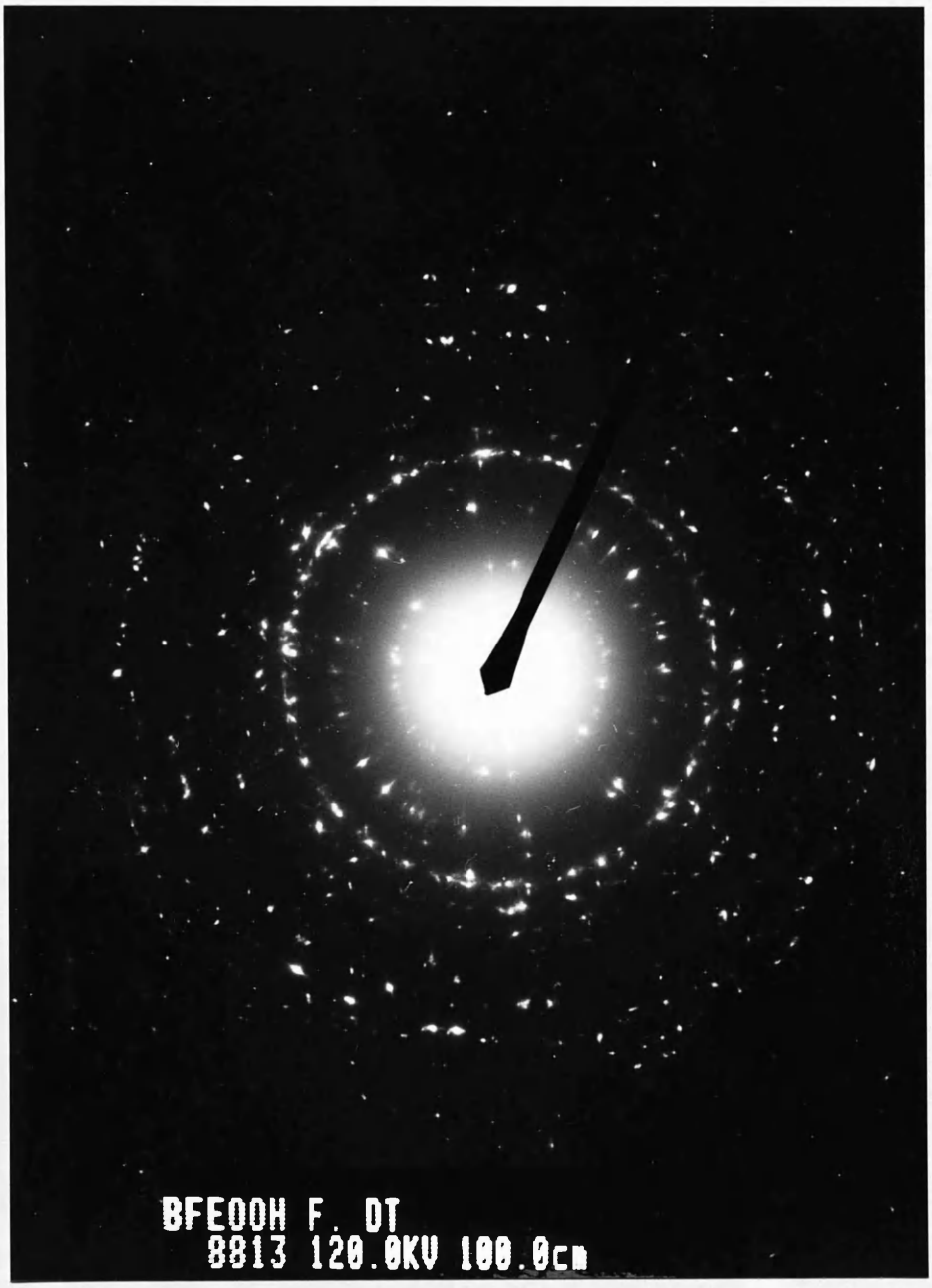

PLATE 8

Electron Diffraction Pattern of βFeOOH(F)

d-spacings given in Table 3.1

PLATE 9

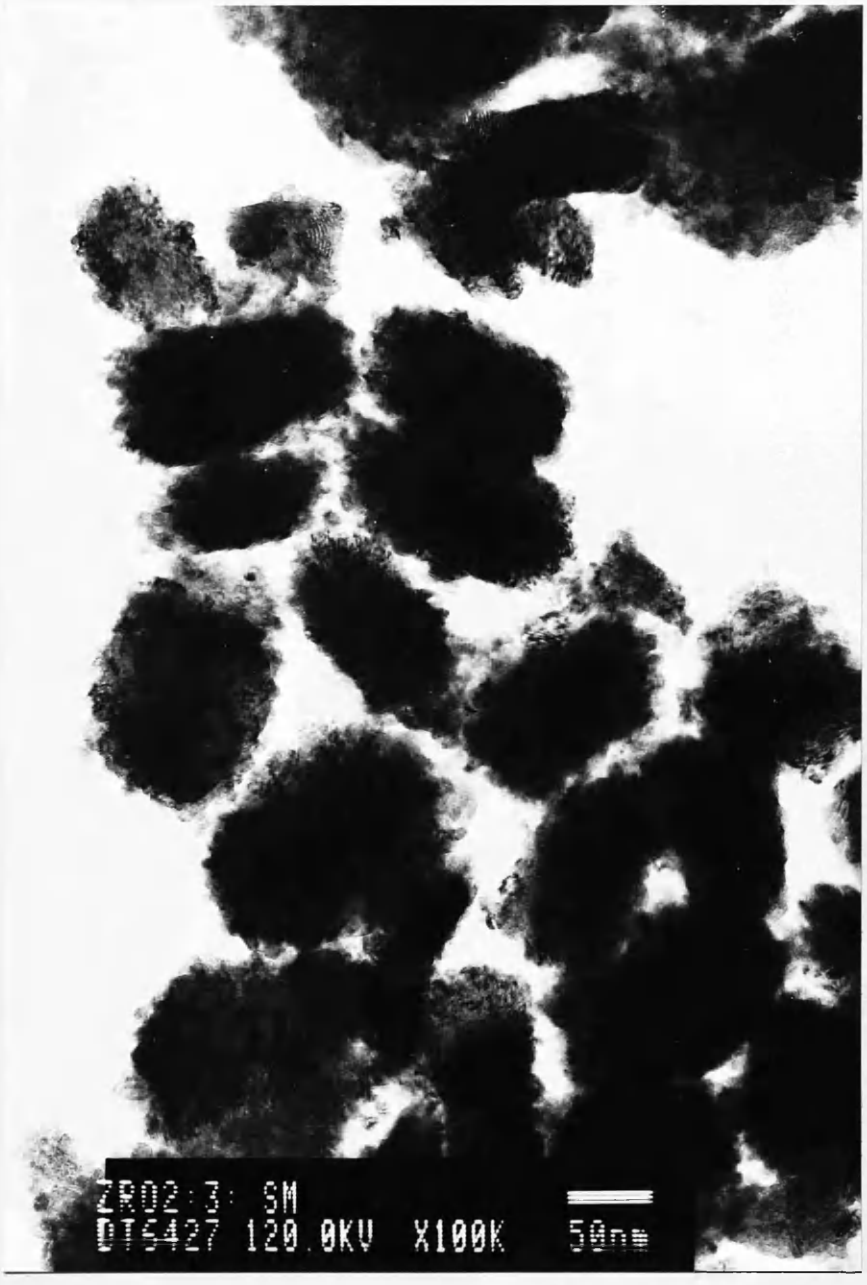

PLATE 9

Electron Micrograph of Monoclinic Zirconia (ZrO_2)

Prepared by the method of Clearfield (7)

PLATE 10

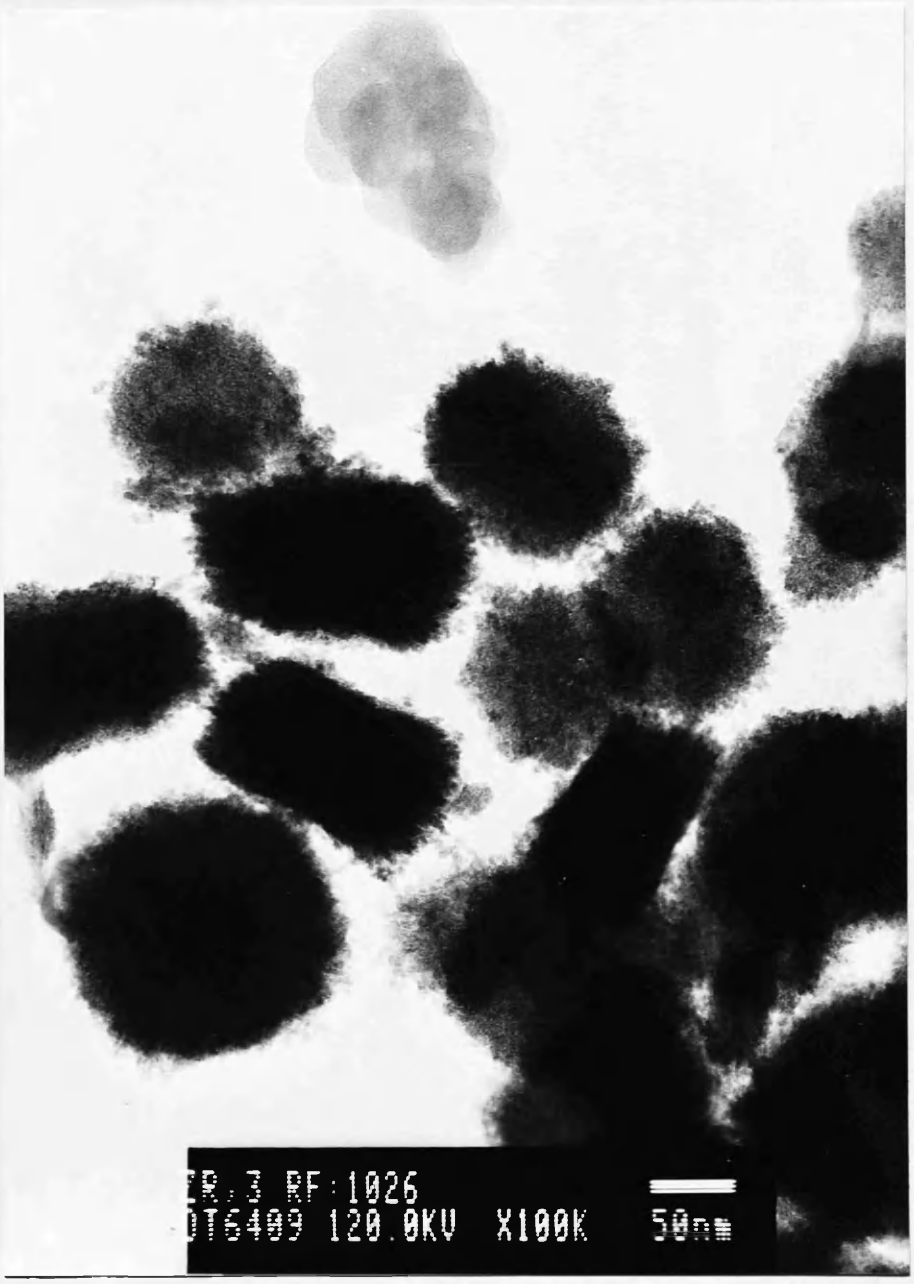

PLATE 10

Electron Micrograph of ZrO_2 (F). A sample of ZrO_2 equilibrated with sodium fluoride

PLATE 11

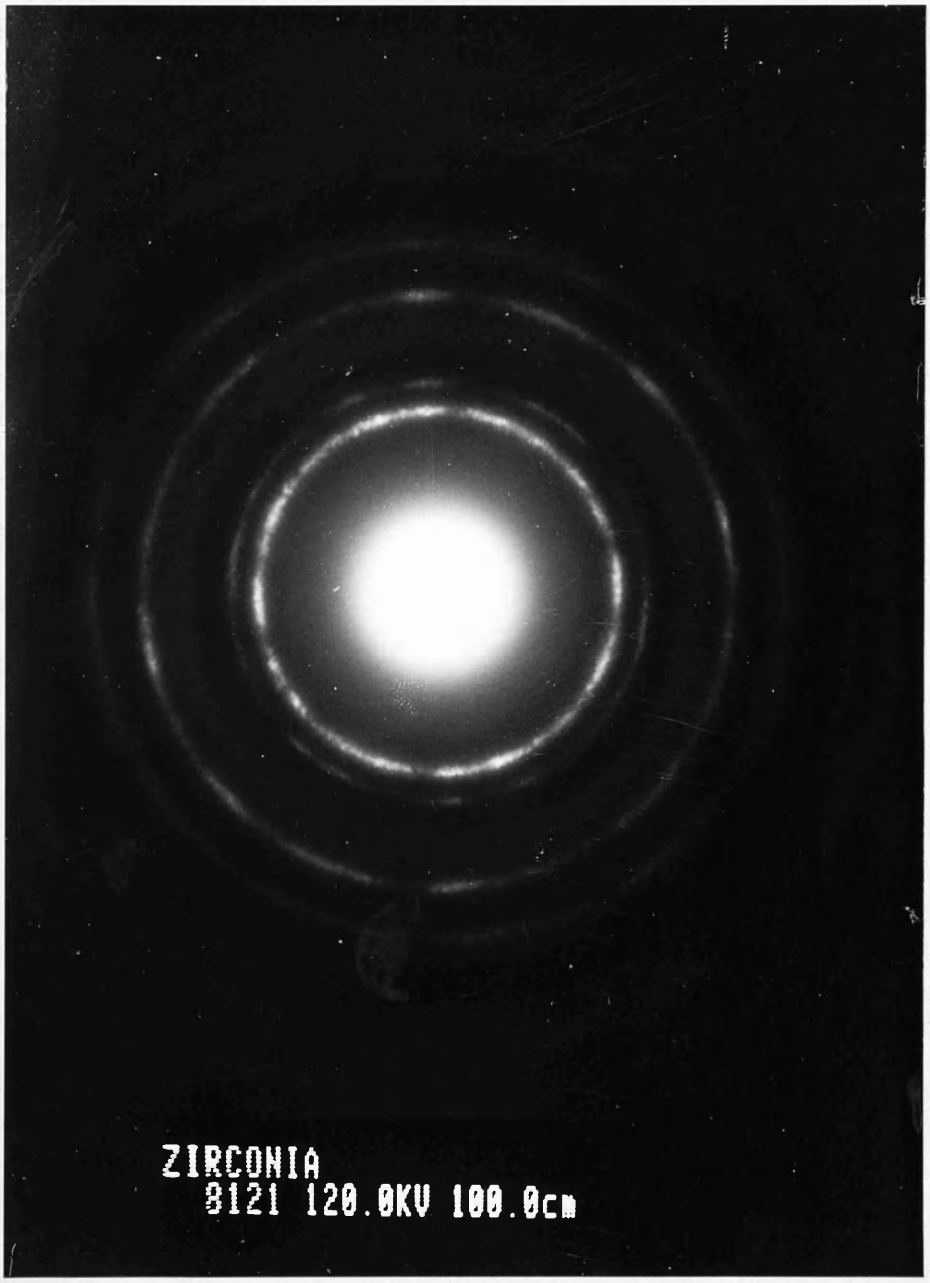

PLATE 11

Electron Diffraction Pattern of ZrO_2

d-spacings given in Table 3.2

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CHAPTER 4

CALIBRATION AND USE OF ION SELECTIVE ELECTRODES

Introduction

A titrimetric analysis of any crystalline colloidal dispersion depends fundamentally upon the response of the sensors. The most useful sensors are ion selective electrodes of which the hydrogen glass electrode was the first and is still the most widely used.

4.1 History of Ion Selective Electrodes

Ion selective electrodes (ISEs) have become one of the most useful tools for rapid analysis or on-line monitoring in contemporary analytical chemistry. Their history begins with the electrochemistry of membranes (semi-permeable, liquid and porous), then the development of the glass electrode, leading to electrodes based on various crystalline materials. From the mid-nineteenth into the twentieth century, Gibbs, Arrhenius, Nernst, Planck and Ostwald formulated the first adequate theories of electrolyte solutions and explanations of their thermodynamic properties. In the early 1900's, Cremer found that when a thin membrane of glass was interposed between two aqueous solutions, an electric potential difference was observed which was very sensitive to changes in acidity (1). This "glass electrode potential" was further characterised by Haber and Klemensciewicz in 1909 and shown to depend quantitatively on the hydrogen ion concentration (2). Although, this phenomenon was not fully understood until an adequate theory of equilibrium for ions across interfaces was developed by Donnan (3). An ideal or

Nernstian electrode response will be obtained when only one ion enters into a Donnan equilibrium at the membrane/solution interface. Nikolsky and Tolmacheva extended these studies with the theory of the glass membrane; that no ions other than those composing the membrane go through, and the potential is a result of the ion transport through the membrane (4). This effect is achieved by introducing some ion selectivity into the structure of the membrane material. Von Lengyel and Blum demonstrated conclusively that a Nernstian response to sodium ion could be obtained upon the introduction of Al_2O_3 or B_2O_3 into a glass (5). The necessity of taking diffusion potentials inside the glass membrane into account lead Eisenman, Rudin and Casby (6) to maximise sodium specificity in sodium aluminosilicate glass composition. These observations suggested that practical electrodes of specialised glass composition might be specifically selective to cations such as Na^+, K^+, Ag^+, NH_4^+, Tl^+, Li^+ and Cs^+. The more strongly an ion is preferred by such a solid ion exchanger, the more poorly does it move within the membrane; since the more difficult it is to jump from site to site. For this reason, there are opposing effects between mobilities and affinities of ions in a solid ion exchanger, which constitutes a principle limitation of such systems (7). Despite this limitation, solid ion exchangers offer a variety of electrodes suitable for measuring monovalent cations.

The need for more specific additions of carrier molecules to increase the selective properties of

electrodes particularly for measuring divalent cations (8) and a variety of anions (9) progressed to the use of liquid ion exchangers. These are membranes composed of a water-immiscible solvent interposed between two aqueous solutions. Their history has been summarised by Shean and Sollner (10). When such membranes contain an appreciable concentration of an ionisable species which is preferentially soluble within the membrane, they function as liquid ion exchangers (11) which differ from solid ion exchangers in that the ion exchange sites are free to move within the membrane.

Specific sequestration of cations by neutral macrocyclic molecules (12), typically cyclic antibiotics and polyethers, was the next step in ion selective electrode development. These offer the possibility of exquisite selectivity, comparable to the characteristics of biological membranes. The mechanism by which these uncharged molecules produce such highly specific electrodes in a phospholipid bilayer membrane is due to their action as specific solubilisers of cations within the liquid-like interior of the membrane (13). These molecules, sometimes called 'neutral carriers', are devoid of charge, but contain an arrangement of ring oxygens energetically suitable to replace the hydration shell around cations, for example, the valinomycin electrode for potassium measurements (14).

In parallel, attempts were made to design a membrane electrode based on crystalline materials. Kolthoff and Sanders studied the potential generated by electrodes involving pure silver halide membranes (15). E_o values

were found for chloride, iodide and bromide solid state electrodes. Their experiments upheld the Nernstian behaviour of these electrodes in which the slopes were just slightly less than theoretical values. The first real success in this area stems from the development of the ion exchange membrane composed of a single crystal by Frant and Ross (16). Their LaF_3 ion selective electrode for fluoride determination along with the glass electrode and the valinomycin electrode for potassium are still the most successful products in this field. A critical and wide ranging view of precipitate based ion selective electrodes is given by Pungor and Toth (17).

From the preceding discussion, it is evident that all ion selective electrodes are similar in mechanism and in the way they are used. They differ only in the details of the process by which the ion that is to be determined moves across the membrane and by which other ions are forbidden access to the membrane.

In the initial studies in this laboratory on the ion exchange behaviour of amphoteric inorganic oxide hydroxide dispersions, the hydrogen electrode was used exclusively in the titration procedure. In this particular research, the number of ion selective electrodes was expanded to include essentially all the ions which were in solution and capable of exchange or sorption interactions with the crystals. The reliability of these electrodes was fundamental to the validity of any titrational procedures used. Consequently, only reliable electrodes were chosen and methods were devised in which the response could be verified under

conditions close to those obtained in the titrational assembly. Particularly, hydrogen, chloride, iodide, bromide, sodium and fluoride electrodes were used.

4.2 Theory of Membrane Potentials

The theory of the origin of membrane potential of electrodes begins with the solution of the flux equations for liquid junctions by Planck (18) and Nernst (19). This was first applied to semipermeable membranes by Teorell (20,21) and by Meyers and Sievers (22) by including the effects of Donnan equilibria at the membrane-solution interfaces. Helfferich (23) and Mackay and Meares (24) extended the analysis to include boundary conditions appropriate to ion exchangers. Karreman and Eisenman (25) obtained analytical expressions for the glass electrode potential in terms of the ion exchange equilibrium constants and mobilities of the cation species characteristic of the glass.

A Nernst potential is observed when a membrane separates two solutions of a single salt at two different concentrations:

$$E = (RT/z_iF) \ln (a_i' / a_i'') \qquad \text{Eq.[4.1]}$$

where a_i' and a_i'' represent the activities of the ion, i, in the two aqueous solutions on either side of the membrane. R is the gas constant, T is absolute temperature, z_i is the charge of the ion, including sign, and F is the Faraday constant.

If the interior of an ion selective electrode is filled with a solution of a salt of constant composition, the electric potential, E, measured using such a half cell depends only on the activity of the ion, i, in the external solution. Changes in this membrane potential can be measured by making electrical contact to the inner solution with a suitable reference electrode, and at the same time contacting the sample solution with a second reference electrode via a salt bridge. A high input impedance voltmeter connected across the two reference electrode leads will complete the electric curcuit and indicate a potential:

$$E_{cell} = \text{Constant} + (RT/z_iF) \ln a_i \qquad \text{Eq.[4.2]}$$

The constant term depends on the choice of reference electrodes used, the choice of ion activity in the inner solution and also a small potential associated with the liquid-liquid junction at the salt bridge connection. RT/F is the Nernst factor and has a value of 59.16 millivolts at 25° C.

$$E_{cell} = E_o + (.05916/z_i) \log a_i \qquad \text{Eq.[4.3]}$$

The constant term described above is defined as E_o. For future actions E will be referred to as the potential of the cell. The ion activity, a_i, is defined as the product of the molar concentration, c_i, and the corresponding ion activity coefficient, γ_i.

$$a_i = c_i \gamma_i \qquad \text{Eq.[4.4]}$$

In 1921 it was observed by Lewis and Randall (26) that in dilute solutions the activity coefficient of any ion depends solely upon the total ionic strength of the solution. The principle of specific ion interaction was stated by Brønsted (27) in 1922 which requires that all ions in mixed electrolyte solution be considered in calculating charge density throughout the solution. This is accomplished by including all ions present in the sum:

$$I = 0.5 \Sigma c_i z_i^2 \qquad \text{Eq.[4.5]}$$

which completes the definition of ionic strength, I. This value is needed in order to calculate the activity coefficient, γ_i. Although single ion activity coefficients are not strictly defined in thermodynamics, the Debye-Hückel interionic attraction theory (28) includes an expression for such activity coefficients. In any potentiometric cell it is possible to combine these single activity coefficients in such a way that only thermodynamically defined, mean molar activity coefficients appear in the final expressions.

$$-\log \gamma_i = A z_i^2 \sqrt{I} / (1 + Ba \sqrt{I}) \qquad \text{Eq.[4.6]}$$

The constants, A = 0.51 and B = 0.328, are applicable to solutions at 25° C. The effective diameter of the hydrated ion, a, is approximately 3 Å for most singly charged ions

(29) so that, for these species, the denominator of the Debye-Hückel equation reduces to $(1 + \sqrt{I})$. From this equation Davies (30) developed an empirical extension to calculate activity coefficients:

$$-\log \gamma_i = 0.51 z_i^2 \left(\sqrt{I}/(1+\sqrt{I}) - 0.3I\right) \qquad \text{Eq.[4.7]}$$

While the Debye-Hückel equation is limited to ionic strengths below 0.02M the Davies equation gives accurate estimates of the activity coefficients over a range from infinitely dilute solutions to ionic strengths of 0.1M.

A thorough calibration (see Section 4.5) of each ion selective electrode determines the slope, or Nernst factor, and E_o for each electrode system. Upon measurement of an unknown the potential indicated is converted, with the use of slope and E_o, into the ion activity, a_i, by solving the Nernst equation (Eq.[4.3]). Awareness of the particular ionic environment allows calculation of the ionic strength (Eq.[4.5]). Substitution of ionic strength into the Davies equation (Eq.[4.7]) gives the activity coefficient, γ_i. The molar concentration, c_i, can be determined at any time by the division of the ion activity with the activity coefficient (Eq.[4.4]).

4.3 Structure of Ion Selective Electrodes

4.3.1 pH Electrode

The pH glass electrode measures the activity of hydrogen ions in solution. A diagram of a pH electrode is shown in Fig. 4.1. The potential at the glass solution interface is a consequence of the exclusive exchange of hydrogen ions between the test solution and the hydrated surface layer of the glass membrane. An internal contact is made with a chlorodised silver wire dipping into a chloride containing pH buffer inside the glass bulb. A constant stable potential is maintained at the internal glass buffer interface and between the chloride in the buffer and the chlorodised wire. The electrical potential for the bulb assembly, therefore contains only one variable; the hydrogen ion activity of the external electrolyte, as Eq. [4.3].

For many years the typical glass composition consisted of 22% Na_2O, 6% CaO, 72% SiO_2 (31). More recent advances in the use of lithium based glass have eliminated some problems at alkaline pH's that were caused by the interference of sodium and potassium ions.

4.3.2 Sodium Electrode

The sodium electrode is identical to the hydrogen electrode except that a small change in the composition of the responsive glass changed the selectivity from hydrogen to sodium ions most remarkably (5).

4.3.3 Chloride Electrode

The chloride electrode is a different class of electrodes, it is a crystalline solid state device that measures chloride ion in solution. The electrode's sensor is a pellet pressed from a co-precipitated mixture of silver chloride and silver sulfide bonded into an epoxy body (see Fig.4.2). The silver sulfide is added to increase electrical conductivity. Silver ions act as the charge carriers in the pellet, responding to changes in silver ion activity with a Nernstian slope. The effect of variation of chloride ion activity in the test solution is detected through its effect on silver activity via the solubility product of the silver chloride. Iodide and bromide electrodes work on the same principles. The internal contact to this pellet is made with a chloride solution saturated with silver into which is dipped a chlorodised silver wire.

4.3.4 Fluoride Electrode

The fluoride electrode, devised by Frant and Ross in 1966 (16), is one of the most successful ISEs ever developed. The valinomycin electrode is the only other comparable one, but it has a shorter lifetime due to chemical instability. The fluoride electrode employs a single crystal of lanthanum trifluoride that is doped with small percentages of europium impurities to increase the conductivity but leaves membrane function unaffected. Fluoride ions are mobile within the crystal lattice of LaF_3 and are rapid to establish equilibrium with free fluoride

ions in solution. The single crystal is set in an epoxy resin tube (see Fig.4.2) while the internal contact is made with a chlorodised silver wire in an inner solution of 1 M KF saturated with KCl and AgCl.

4.3.5 Reference Electrode

The reference electrode used in these experiments was of the double junction, silver/silver chloride type (see Fig.4.3). This construction includes an inner chamber with a chlorodised silver wire in contact with a potassium chloride solution saturated with silver chloride (Orion 90-00-02). The inner chamber is connected to an outer chamber containing 10% potassium nitrate (Orion 90-00-03) by a ceramic frit. Contact with the solution to be measured is made through a sleeve-type junction. The importance of the design of this reference electrode cannot be overestimated. It must provide stable, reproducible potentials free from large junction effects. The equitransferent KNO_3 solution (i.e. equal transport numbers) and the large area of contact with the measuring solution, provided by the sleeve-type junction which prevents clogging problems due to the larger flow, reduces junction potential and as a result this electrode is found to be particularly suitable.

FIGURE 4.1 DIAGRAM OF A pH ELECTRODE

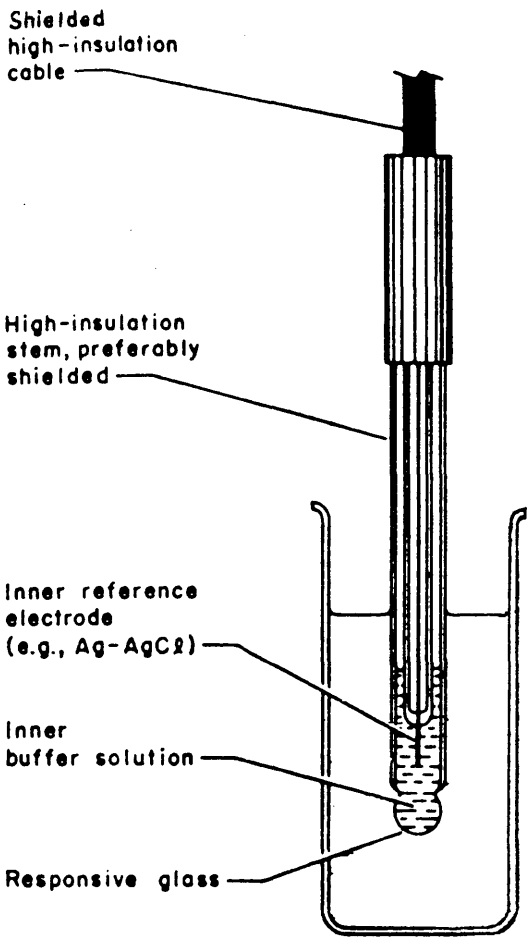


FIGURE 4.2 DIAGRAM OF A HALIDE ELECTRODE

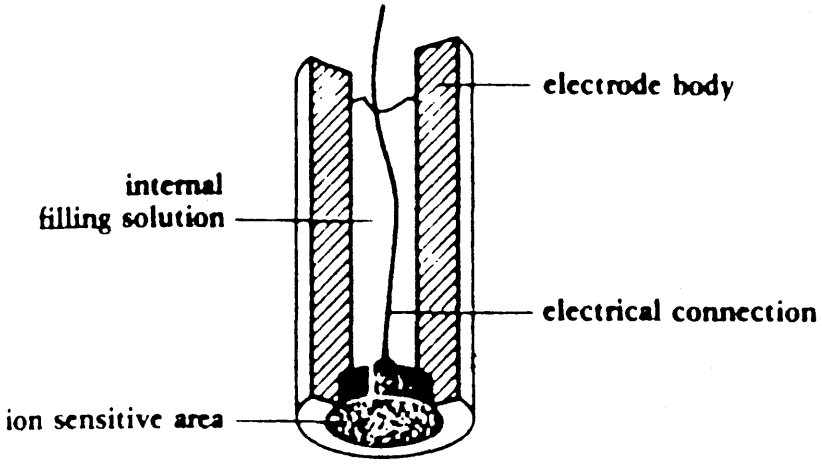
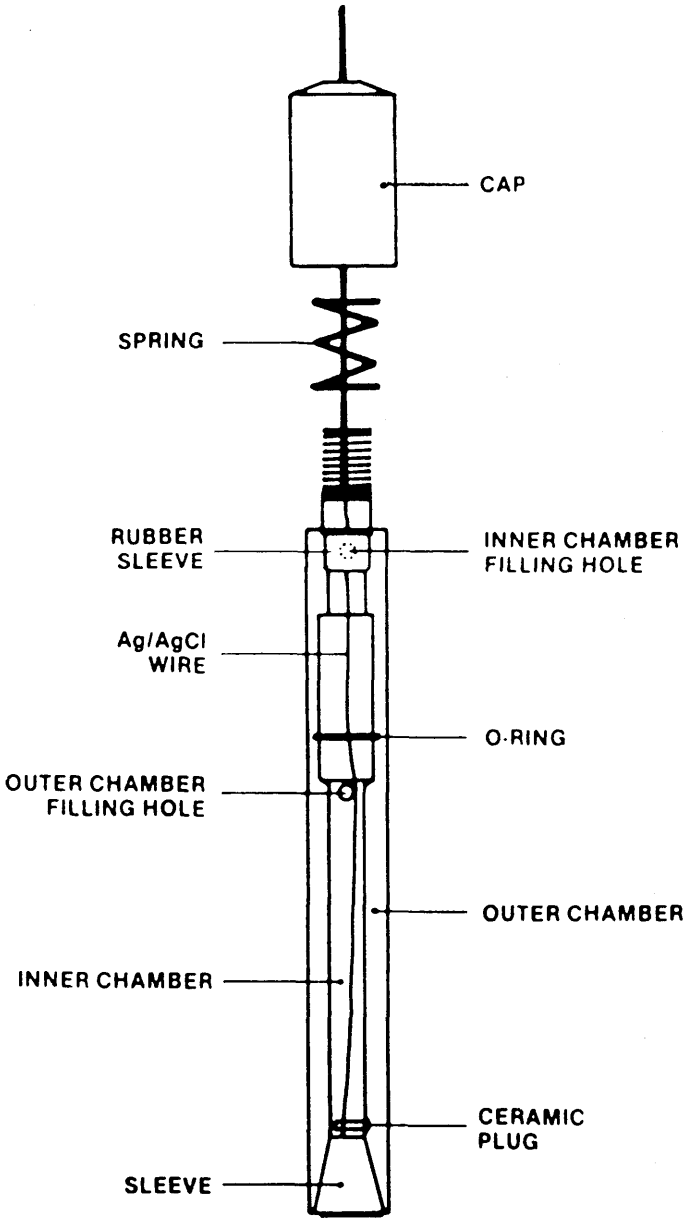


FIGURE 4.3 DIAGRAM OF A DOUBLE JUNCTION REFERENCE ELECTRODE



4.4 Electrode Preparation

A great deal of care has to be taken in the calibration and the pre-treatment of ISEs to obtain the best results. In order to assure optimum electrode performance a series of tasks were carried out the day before each experiment. This procedure enabled the electrodes to 'settle down' overnight and prevent large junction potential deviations during an experiment. Combination electrodes are convenient, but for precision work it was considered necessary to use a single reference for all the electrodes involved. Each electrode used and its corresponding preparation was as follows:

4.4.1 Double Junction Reference Electrode (Orion model no. 90-02)

The folowing procedure would be performed about once a week if the electrode was used frequently in many colloidal dispersions. The inner and outer filling solutions must be drained and reassembled. The following instructions refer to Fig. 4.3. The cap was unscrewed and the spring slid up the cable. The top of the electrode body was pushed down with the thumb until the inner cone was released from the sleeve. The cone was withdrawn from the sleeve with a gentle twisting motion, using a tissue, and the body and sleeve rinsed with distilled water. The rubber sleeve at top of inner chamber was slid down to uncover the filling hole. The inner chamber was filled with Orion 90-00-02 coloured filling solution, using a flip-spout bottle, and the sleeve slid back up. The spring and cap were placed

back on the inner chamber and screwed on finger tight. Using Orion 90-00-03 outer chamber filling solution a small amount was added through the filling hole in the outer sleeve. The electrode was tipped to moisten the green O-ring on the electrode body. The electrode was held by the cap in one hand, the outer sleeve pushed up to the cap with the other hand, allowing the solution to wet the inner cone. The sleeve was released and checked to see that the end of the sleeve was flush with the bottom surface of the cone, and the outer chamber was filled up to the filling hole. The electrode was stored upright in a standardising solution.

4.4.2 Hydrogen Electrode (Russell Model SWL)

If the glass electrode response became sluggish or calibrated with a low slope, the following procedure was performed using a glass etching solution which removed the hydration layer on the surface of the glass. This was prepared from a solution that was 1 M in acetic acid and 0.1 M in sodium fluoride. The electrode was immersed in the etching solution for 1-2 minutes and then rinsed with distilled water. The electrode was then stored in distilled water overnight.

4.4.3 Chloride Electrode (Orion model no. 94-17B)

The surface of this solid state electrode passivated in time, causing drift and loss of response at low chloride levels. The electrode was restored by repolishing with an

abrasive strip. Under experimental conditions used in this research it deemed necessary to polish this electrode about once a month. The electrode was held with the membrane facing upward. A few drops of distilled water were placed on the membrane surface. Using light finger pressure the abrasive Ultralap 3 micron aluminum oxide strip was placed on the membrane and rotated for about 30 seconds. The electrode was rinsed and stored in a 10^{-5} M standard sodium chloride solution before use. The iodide and bromide solid state electrodes were restored in the same manner.

4.4.4 Sodium Electrode (Orion model no. 97-11-00)

The sodium electrode must never be stored in air or distilled water. Prior to use it can be etched with .1 M sodium fluoride etching solution as described for the hydrogen electrode above. It should then be stored in a standardising solution overnight.

4.4.5 Fluoride Electrode (Orion model no. 94-09)

The fluoride electrode consists of a single crystal lanthanum fluoride membrane. It should be stored in a standardising solution overnight before use and stored in air if out of use for longer periods of time. The protective rubber cap should be replaced when storing in air to prevent accidental damage to the sensing crystal.

4.5 Calibration of Ion Selective Electrodes

This research depended upon the reliability of ion-selective electrodes and, therefore, considerable attention was given to their calibration. Apart from the hydrogen ion electrode which was calibrated by buffers described below, all other ISEs were calibrated with a ten to twenty point calibration curve that was derived by titrating aliquots of specific electrode standards into a water jacketed beaker controlled to 25 °C. This calibration was repeated before and after each experiment to test for accuracy of each ISE during a run. A titration of an oxide hydroxide crystalline dispersion could take up to three hours so it was important to check that the electrodes had not drifted significantly during that period of time. Repeated calibrations which displayed more than a 2 mV drift, in its standardising solution before and after each titration, were considered unsuitable and that experiment was rejected for quantitative analysis. Calibrations were conducted under conditions in which the electrodes would be used during a titration. Questions about the effect of pH and ionic strength variations during the calibration compared to the titration of the oxide hydroxide were answered by the ISE responses in the control experiment (see Section 5.3.1). The control titration was the ultimate test of the stability of the electrodes within certain pH and ionic strength ranges. If the mass balance of ions in solution are known, when there are no ion exchange crystals present, then the mass balance must be obtained. The control experiment shows conclusively that

the calculation methods used (see Section 5.2.1) take electrode potentials directly to a concentration of the ion involved that is valid.

The hydrogen electrode was calibrated with eight internationally accepted pH buffers described in Table 4.1. These were chosen to cover the pH range expected to be monitored during an oxide hydroxide titration. The buffers were placed in thermostatted jacketed beakers at 25 °C and the electrode mV reading was recorded. These values were inputted into the ISE calibration equation program (Appendix P4.2).

It proved convenient to calibrate sodium and chloride electrodes concurrently using a sodium chloride standard solution. Generally, this was chosen up to 10 ml, delivered from a grade-A microburette, of 0.1 M NaCl into an initial volume of 50 ml distilled water or solution of known ionic strength. These concentrations covered the range of sodium or chloride seen by the electrodes during an experiment with crystals present. The sodium chloride standard solution was made up from Analar reagent and analysed by Gran plot technique (see Appendix C4.3). The fluoride electrode was calibrated similarly, except using 0.1 M sodium fluoride as the standard solution. This solution was analysed by an ion exchange technique (see Appendix C4.4).

Millivolt readings were recorded from the Orion Ionalyzer Model 940 meter and Orion Model 607 electrode switch. These readings were used in a calibration computer program (see Appendix P4.2) which calculated both first and

second order curve fits of E_{cell} versus log a_i ([Eq. 4.2]) from the data. Therefore, an experimental linear equation was derived for each electrode on that particular occasion. Hence, before an experiment was begun, calibration data could be surveyed and satisfactory electrode behaviour confirmed. An electrode with a calibrated slope below 57 mV/decade was rejected. The solutions for the first and second order curve fits for each electrode calibration were read into a computer data file for the corresponding experiment. All mV readings were associated to their calculated activities using the curve fit solutions from the calibration data. These curve fit equations are given in Tables 4.2 to 4.5 for the chloride, sodium, hydrogen and fluoride electrodes, respectively. Their computed curve fit data solutions and corresponding -log a_i were compared to the corresponding function -log a_i determined from the calibration emf values and activity coefficients from Eq.[4.7]. Tables 4.2 to 4.5 show the first and second order curve fit deviations in % error. In the majority of cases the linear relationships were satisfied and the use of the second order curve fitting equation was not required.

In the calibrations, ionic strengths were as in the actual experiment. In a manner similar to that described in Section 4.2, activities were calculated from the concentration data using the Davies equation (Eq.[4.7]). To demonstrate the effects of ionic strength the data obtained from the calibrations were plotted as emf versus -log c_i and -log a_i. Typical plots for the chloride and sodium electrodes are shown in Fig. 4.4 and Fig.4.5

respectively. The effect of increasing concentration and subsequent increasing ionic strength can be seen in the non linearity of emf versus -log c_i. Therefore calibration equations based on the -log a_i will be used. Typical calibration graphs for the fluoride and pH electrodes are given in Fig. 4.6 and 4.7 respectively.

This calibration system had three major advantages. Firstly, the additions from the burette caused small volume increases and minimised any possible temperature excursions. Secondly, by using the same standard solution and the same burette during the titration with crystals present which followed, accuracy was increased. Thirdly, the increased number of calibration data points made it possible to determine a meaningful first and second order best-fit line equation using the least squares method (see Appendix P4.2).

Table 4.1 Preparation of Buffer Solutions

Eight international standard buffer solutions (32) for calibration of the hydrogen glass electrode were prepared as follows:

pH 1.50; dissolve 1.864g KCl in 200 ml distilled water, add 20.7 ml of 1 M HCl and dilute to 500 ml in a volumetric flask.

pH 3.00; dissolve 5.1055g KHP ($COOH.C_6H_4.COOK$) in 200 ml distilled water, add 11.5 ml of 1 M HCl and dilute to 500 ml in a volumetric flask.

pH 4.00; dissolve 5.1055g KHP in 200 ml distilled water, add 0.5 ml of 0.1 M HCl and dilute to 500 ml in a volumetric flask.

pH 7.00; dissolve 3.0285g Tris ($C_4H_{11}O_3N$) in 200 ml distilled water, add 23.3 ml of 1 M HCl and dilute to 500 ml in a volumetric flask.

pH 9.00; dissolve 3.0285g Tris in 200 ml distilled water,add 28.5 ml of 0.1 M HCl and dilute to 500 ml in a volumetric flask.

pH 10.00; dissolve 2.384g $Na_2B_4O_7.10\ H_2O$ in 200 ml distilled water, add 91.5 ml of 0.1 M NaOH and dilute to 500 ml.

pH 11.00; dissolve 1.7745g Na_2HPO_4 in 200 ml distilled water, add 20.5 ml of 0.1 M NaOH and dilute to 500 ml.

pH 12.00; dissolve 1.7745g Na_2HPO_4 in 200 ml distilled water, add 134.5 ml of 0.1 M NaOH and dilute to 500 ml.

Table 4.2 Chloride Electrode Calibration Data

FILE NAME = CL187

FIRST ORDER EQUATION $E = -17.247 + 58.757\ pCl$

SECOND ORDER EQUATION $E = -18.223 + 59.498\ pCl + -0.135p\,[Cl]^2$

N	E mV	pCl (actual)	pCl 2ND ORDER	pCl 1ST ORDER	% error 2ND ORDER	% error 1ST ORDER
1	176.9	3.304	3.304	3.304	-0.1	-0.1
2	159.3	3.008	3.004	3.005	0.9	0.8
3	149.7	2.836	2.841	2.841	-1.1	-1.2
4	141.8	2.715	2.706	2.707	1.9	1.8
5	137.0	2.621	2.625	2.625	-0.8	-1.0
6	120.0	2.333	2.336	2.336	-0.6	-0.7
7	110.2	2.167	2.169	2.169	-0.4	-0.4
8	103.3	2.052	2.052	2.052	-0.1	0.0
9	98.0	1.963	1.962	1.961	0.2	0.4
10	82.4	1.697	1.698	1.696	-0.1	0.3

% error = % difference between the actual pCl and the calculated activity

pCl = Negative log of the Cl ion activity

Table 4.3 Sodium Electrode Calibration Data

FILE NAME = NA

FIRST ORDER EQUATION E = 296.971 + -56.665 pNa

SECOND ORDER EQUATION E = 300.466 + -59.638 pNa + 0.602p[Na]^2

N	E mV	pNa (actual)	pNa 2ND ORDER	pNa 1ST ORDER	% error 2ND ORDER	% error 1ST ORDER
1	104.4	3.409	3.405	3.398	1.1	2.5
2	120.6	3.114	3.114	3.113	0.0	0.3
3	130.5	2.942	2.937	2.938	1.2	1.1
4	137.0	2.822	2.821	2.823	0.1	-0.3
5	142.1	2.728	2.731	2.733	-0.5	-1.1
6	146.4	2.653	2.654	2.657	-0.4	-1.0
7	149.9	2.589	2.593	2.595	-0.8	-1.4
8	153.0	2.534	2.538	2.541	-0.8	-1.5
9	155.7	2.486	2.490	2.493	-0.8	-1.6
10	158.0	2.444	2.449	2.452	-1.4	-2.1
11	174.1	2.169	2.166	2.168	0.6	0.1
12	183.1	2.015	2.009	2.010	1.5	1.3
13	189.3	1.911	1.900	1.900	2.4	2.4
14	193.6	1.833	1.826	1.824	1.7	2.0
15	196.8	1.771	1.770	1.768	0.3	0.8
16	199.6	1.721	1.721	1.718	-0.0	0.7
17	201.8	1.679	1.683	1.680	-0.9	-0.1
18	203.7	1.643	1.650	1.646	-1.6	-0.6
19	205.2	1.612	1.624	1.620	-2.8	-1.7

% error = % difference between the actualpNa and the calculated activity

pNa = Negative log of the Na ion activity

Table 4.4 pH Electrode Calibration Data

FILE NAME = PH487

FIRST ORDER EQUATION E = 378.184 + -58.290 pH

SECOND ORDER EQUATION E = 379.958 + -59.042 pH + 0.056p $[H]^2$

N	E mV	pH (actual)	pH 2ND ORDER	pH 1ST ORDER	% error 2ND ORDER	% error 1ST ORDER
1	292.3	1.500	1.487	1.473	3.0	5.9
2	203.6	3.000	2.995	2.995	1.0	1.1
3	142.2	4.000	4.042	4.048	-10.2	-11.8
4	-28.3	7.000	6.960	6.973	8.7	5.9
5	-148.4	9.000	9.026	9.034	-6.1	-8.1
6	-203.0	10.000	9.967	9.971	7.3	6.6
7	-264.5	11.000	11.030	11.026	-7.1	-6.1
8	-320.1	12.000	11.992	11.979	1.7	4.6

% error = % difference between the actualpH and the calculated activity

pH = Negative log of the H ion activity

Table 4.5 Fluoride Electrode Calibration Data

FILE NAME = F187

FIRST ORDER EQUATION $E = -182.118 + 55.611\ pF$

SECOND ORDER EQUATION $E = -187.151 + 60.312\ pF + -1.047p[F]^2$

N	E mV	pF (actual)	pF 2ND ORDER	pF 1ST ORDER	% error 2ND ORDER	% error 1ST ORDER
1	-12.8	3.052	3.053	3.045	-0.2	1.6
2	-28.7	2.757	2.759	2.759	-0.5	-0.4
3	-38.5	2.586	2.580	2.583	1.3	0.8
4	-45.0	2.466	2.462	2.466	0.8	-0.0
5	-49.6	2.372	2.379	2.383	-1.5	-2.4
6	-65.9	2.087	2.086	2.090	0.2	-0.7
7	-75.1	1.923	1.922	1.924	0.2	-0.4
8	-81.5	1.808	1.809	1.809	-0.1	-0.2
9	-86.3	1.721	1.724	1.723	-0.7	-0.5
10	-101.6	1.457	1.455	1.448	0.5	2.1

% error = % difference between the actual pF and the calculated activity

pF = Negative log of the F ion activity

Figure 4.4 Chloride Electrode Calibration Curve

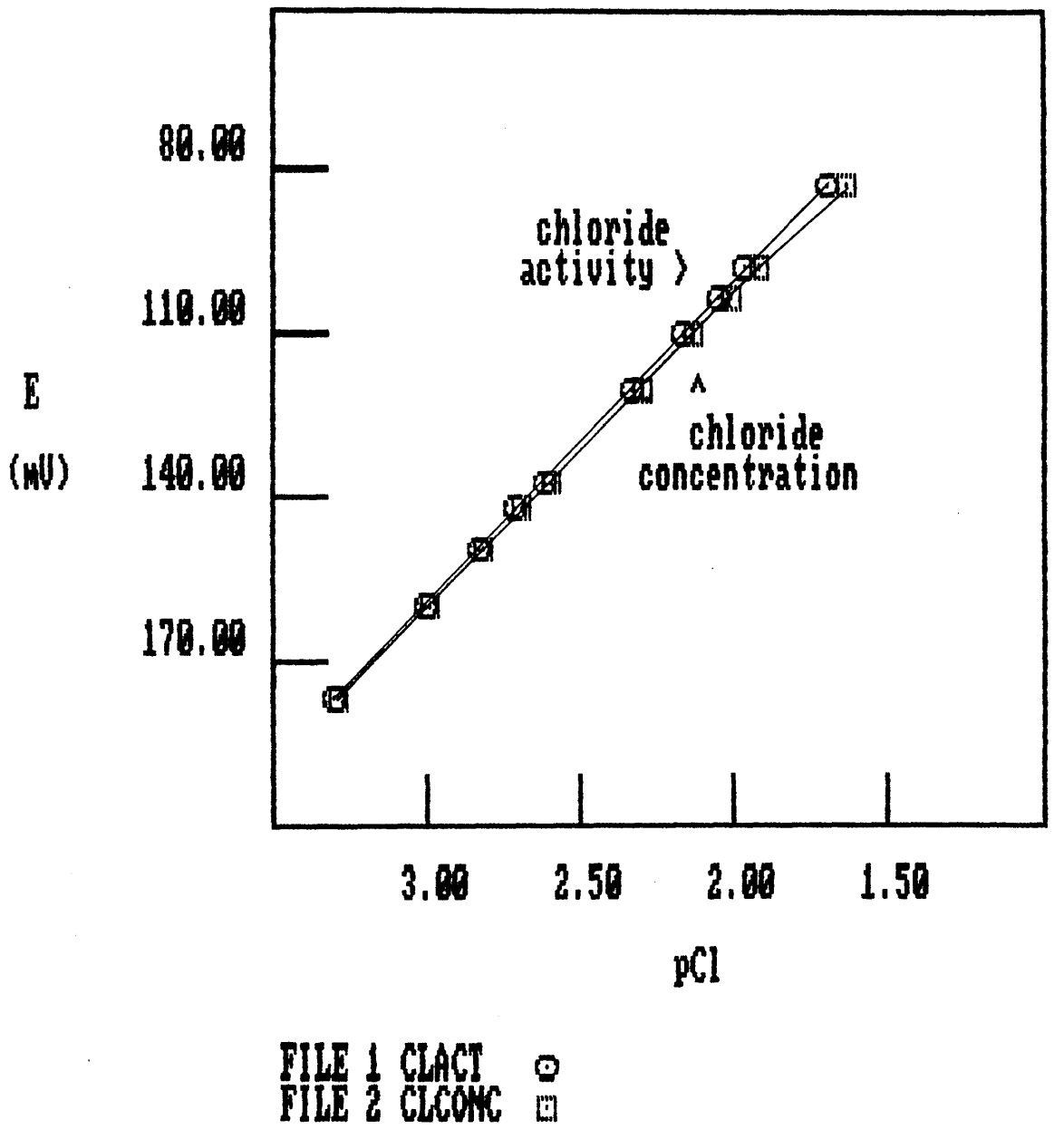


Figure 4.5 Sodium Electrode Calibration Curve

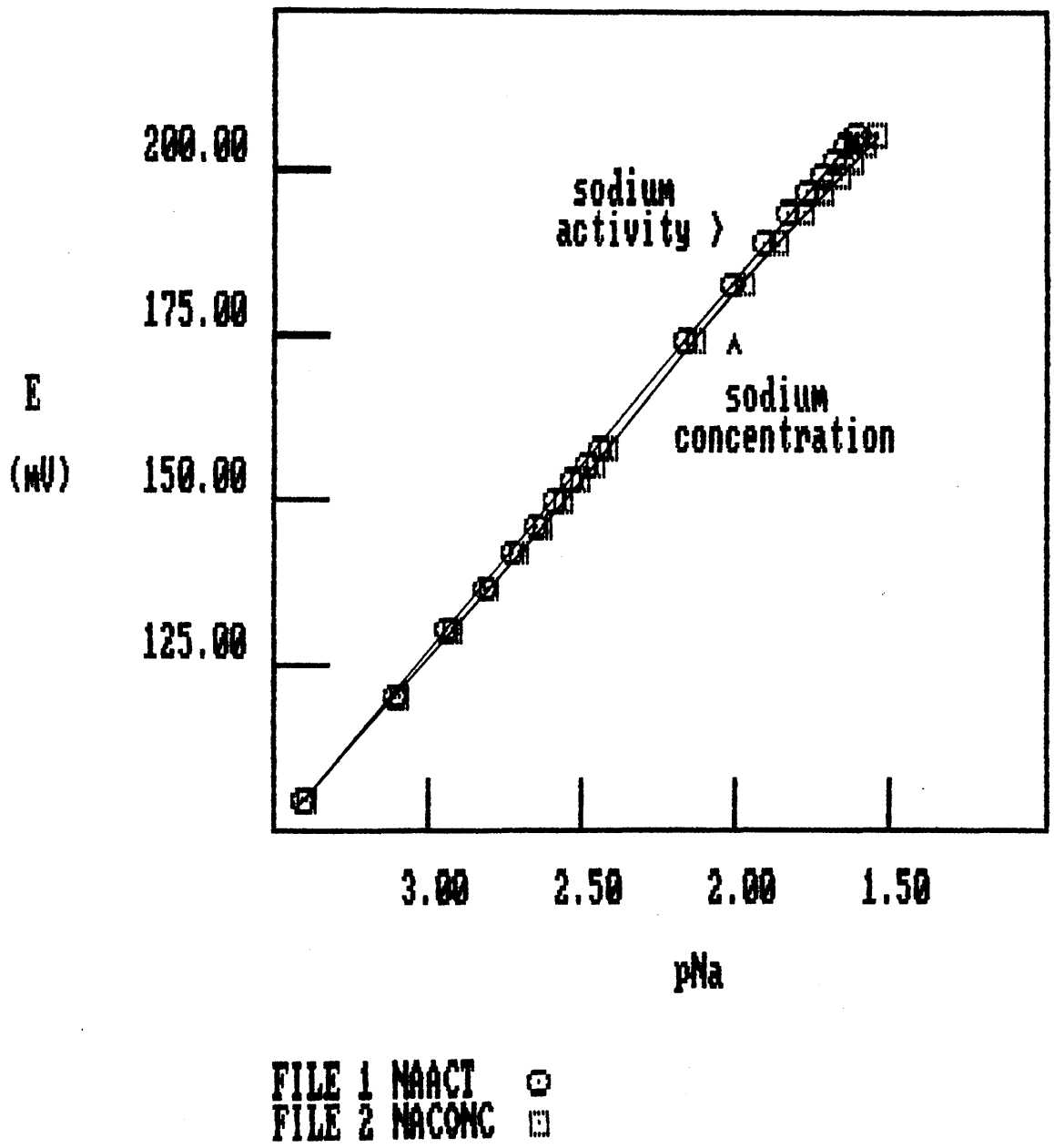


Figure 4.6 Calibration Curve for Fluoride Electrode

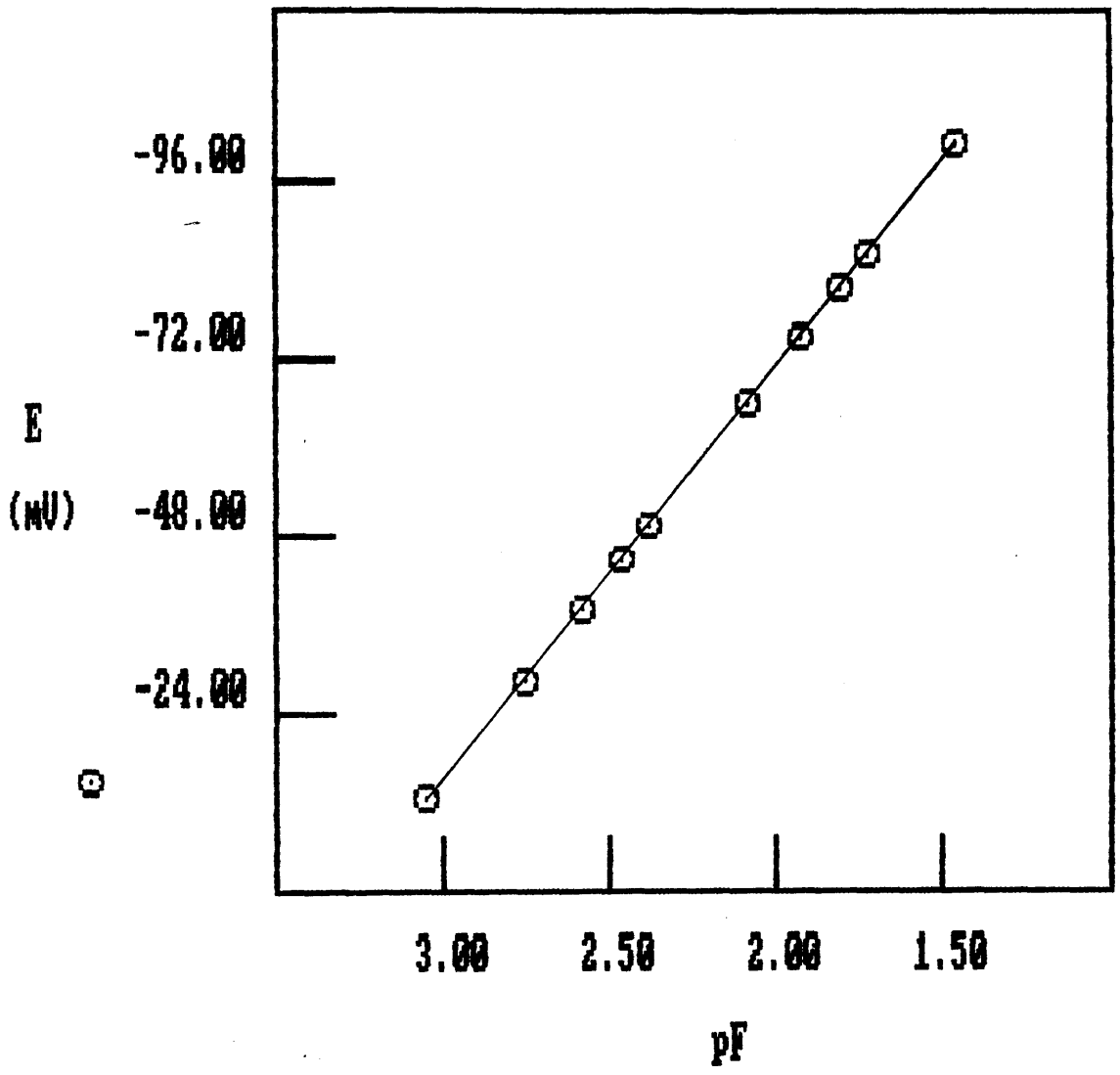
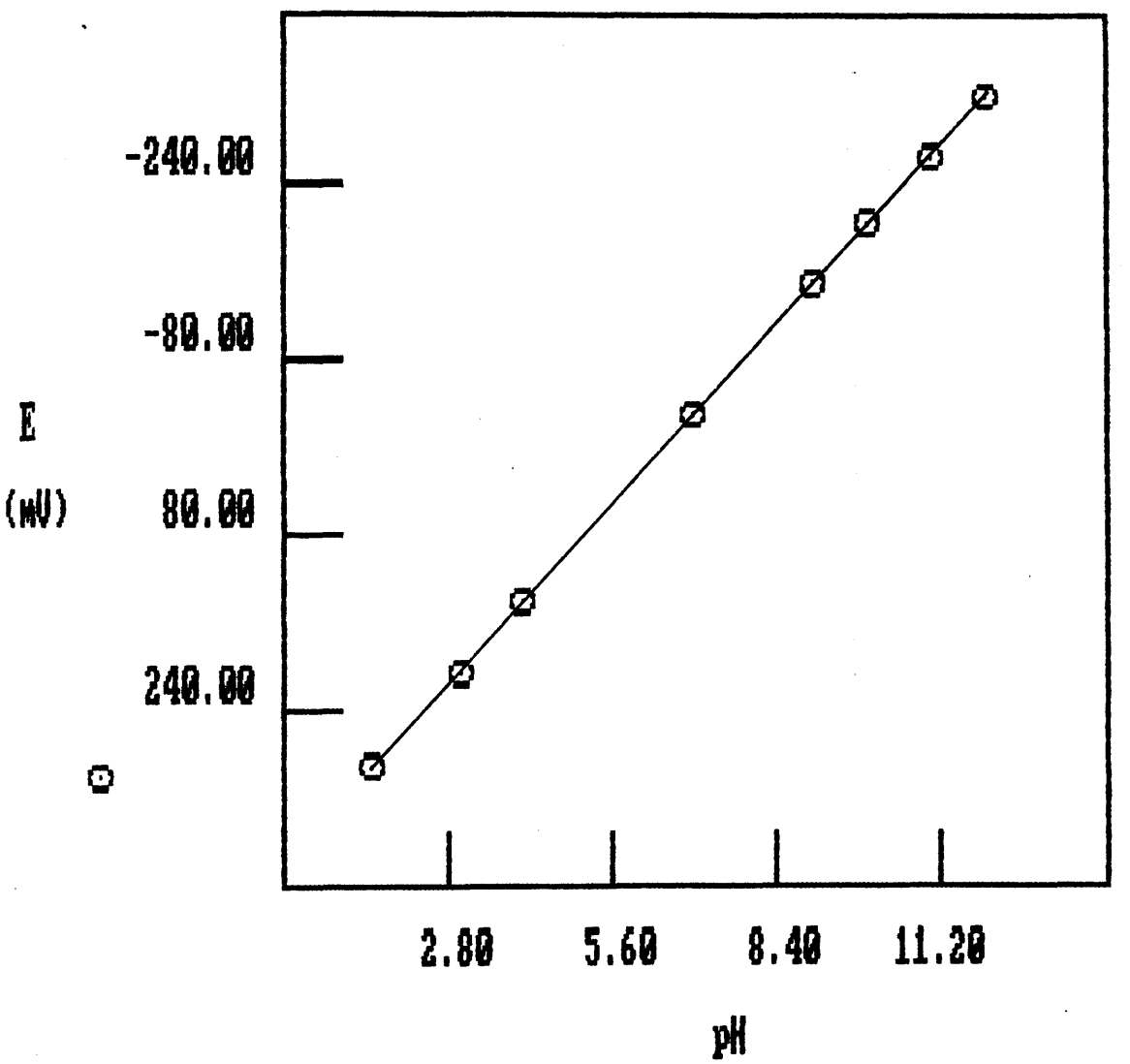


Figure 4.7 Calibration Curve for pH Electrode



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CHAPTER 5

EXPERIMENTAL MULTI-ELECTRODE TITRATION AND COMPUTATIONAL SYSTEM

Introduction

In earlier studies in this laboratory, capacity data were obtained from pH titration (1). In this research, these techniques were expanded by use of a number of ion selective electrodes (see Chapter 4). In this chapter the titrational and computational systems set up to interpret ion exchange and sorption characteristics of oxide hydroxides are described. These methods provide not only support and confirmation of earlier conclusions, but offer new techniques for determining oxide hydroxide ion exchange characteristics as multiionic sorbents.

5.1 Experimental Titration of Oxide Hydroxides

5.1.1 Constant Temperature Bath

A temperature of 25 ± 0.1 ° C was maintained using a toluene-mercury coiled glass thermoregulator in a water tank for all the electrode calibrations and oxide hydroxide titrations carried out in this research. The water was heated by an infra-red light bulb and cooled by circulating tap water using a coiled copper pipe immersed in the tank. The rate of heating and cooling was controlled by the mercury-toluene regulator as a switch to the infra-red light source. As the temperature decreased the toluene density increased and the mercury column shortened. An electronic control system caused the light bulb to be energised when the mercury contact was broken. The opposite effects occured when the temperature increased. This system maintained temperature variation to within ± 0.01 °C with ease.

5.1.2 Ion Selective Electrode Titration

The ion exchange capacities of the oxide hydroxides examined in this work at different pH values were determined using multi-electrode titration procedures. A diagram of the titration cell used is given in Fig. 5.1 and the discussion in this section refers to it. Approximately 0.3 grams of exchanger was dispersed in 20 ml of distilled water and stirred with a magnetic stirrer overnight in the titration cell. The cell was a 50 ml jacketed beaker, thermostated by circulation of 25 °C bath water discussed in Section 5.1.1. A polyethylene beaker inside was fitted with a perspex lid that was used to seal the cell, but contained holes through which pass up to four electrodes, burettes and inlet and outlet tubes for nitrogen gas. The temperature of the system was kept constant at 25 °C. All calibrated electrodes, discussed in Section 4.5, were put into the system. Presaturated 'wet' nitrogen gas was bubbled through the system to avoid the absorption of carbon dioxide from the air. Standard base, acid and salt solutions were added from microburettes in small aliquots as desired. Burettes with very fine capillary tips (medical cannulae) were immersed in the suspension during titration and measurement. The dispersion was stirred with a magnetic stirrer until equilibrium was reached. Emf values were measured with an Orion model EA940 pH meter and model 607 electrode switch. The meter retained individual electrode calibrations in its memory with software that relays mV readings, concentrations, electrode drift or stability in mV/min, last calibration slope and E_o,

temperature, time, date and various timer and print commands. The Orion model 607 electrode switch has the capacity to input up to six electrodes for measurement one at a time. The input jacks are BNC connectors into optically isolated lines, that is, the signal is passed on via an infra red diode, which minimises the effect of possible 'cross-talk' between electrodes. All electrodes were single junction and therefore shared a common reference electrode (see Fig. 4.3). Once equilibrium was obtained the mV reading from each electrode was recorded. These values were used, together with the curve fits of each electrode's calibration (see Section 4.5 and Appendix P4.4), to calculate the ion exchanger's ionic uptake or release.

5.1.3 Control Experiment

An experiment, Table 5.2, was devised to test ISE behaviour at the pH and ionic strengths encountered in a typical titration of the oxide hydroxide crystals. The experiment reproduced the millivolt readings obtained for the hydrogen, chloride and sodium ISEs in a titration of βFeOOH, Table 5.1. It was performed in a 10^{-3} M hydrochloric acid solution without any ion exchange crystals present and sodium hydroxide additions were made as in Table 5.1. The absence of crystals meant there was no unknown 'sources or sinks' of electrolyte. In order to reproduce the same millivolt readings it was necessary to add hydrochloric acid from a burette. This known addition of chloride could then be compared to release of chloride from the βFeOOH exchanger.

5.2 Titration Theory

The following discussion refers specifically to βFeOOH titrations. Modifications to the titration theory and calculation of capacity from the multi-electrode system that were made for monoclinic zirconia, which may be considered a general case, are discussed in Section 7.2.

As prepared, βFeOOH contained leachable hydrochloric acid. When a sample of the crystals was equilibrated with a volume of water, this acid was released in part, reducing the solution pH to approximately 3.5. During titration this equilibrium was successively displaced by addition of sodium hydroxide, hydrochloric acid and sodium chloride. In other experiments, additions of sodium iodide, sodium bromide, sodium perchlorate, sodium fluoride or perchloric acid were made as required. Equilibrium conditions were obtained in a few minutes after addition of reagent to these dispersions and so were suitable for study by a titration technique.

Consider initially only the addition of base to the chloride form of the oxide. Hydrochloric acid in the solution is neutralised, causing release of more acid by the exchanger, by an amount ΔX (mmol/g) from its initial but unknown capacity of X_o (mmol/g). ΔX is therefore the change in capacity of the sample relative to its initial equilibrium value when dispersed in water. The absolute value of capacity, X, corresponding to the amount of chloride/proton uptake per gram FeOOH content at any point in the titration is therefore unknown unless X_o may be found, Eq.[5.1].

$$\Delta X = (X_o - X) \qquad [5.1]$$

For βFeOOH the value of ΔX increased to a constant value in alkaline solutions above pH 10 (1). This was designated ΔX_{max} and indicated that all the acid originally present in the exchanger had been released and neutralised. Therefore from Eq.[5.1], $X_o = \Delta X_{max}$. In this way an absolute scale of capacity was established.

5.2.1 Calculation of Capacity

Consider an initial equilibration of a weight of air dried sample of crystalline βFeOOH, corresponding to G g of FeOOH, with a volume V_o ml of water at 25 °C, yielding an acidic solution. Subsequent additions of B, A, S1 or S2 mmol of base, acid, salt1 or salt2 were made using V_b, V_a, V_{s1} or V_{s2} ml of the respective reagent. Subscripts b, a, s1 and s2 distinguish base, acid, salt 1 and salt 2 respectively.

In the calculation of capacity, X, some assumptions were made. It was assumed that there was negligible Donnan uptake of coion at the ionic strengths used in this work ($I \leq 0.1$). Also, it was assumed that solution volumes were additive so that the total volume of solution, V, is given by Eq.[5.2].

$$V = V_o + V_b + V_a + V_{s1} + V_{s2} \qquad \text{Eq.[5.2]}$$

Since sodium ion is excluded from the exchanger (see Section 6.2.4), its concentration is determined solely by the amount of sodium reagents added (Eq.[5.3]). In this work only sodium hydroxide and sodium salts were employed. Molar concentrations are represented in square brackets and for convenience charges are omitted.

$$[Na] = (S1 + S2 + B)/V \qquad \text{Eq.[5.3]}$$

From the electroneutrality of the solution,

$$[Na] + [H] = [Cl] + [OH] \qquad \text{Eq.[5.4]}$$

In consequence, chloride concentration and ionic strength, I, are defined by Eq.'s [5.5] and [5.6].

$$[Cl] = (S1 + S2 + B + [H]*V - [OH]*V)/V \qquad \text{Eq.[5.5]}$$

$$I = (S1 + S2 + B)/V + [H] \qquad \text{Eq.[5.6]}$$

For these calculations hydrogen ion concentrations were required. Chloride concentrations were inferred from pH measurements (1) during the titration (Eq.[5.5]), but with the introduction of ion selective electrodes to this titration system, halide and sodium concentrations could be determined directly. With pre-calibration, the mV from the ISEs could be converted into concentration readings from each electrode (see Section 4.2). Gain or loss of halide and other ions by the exchanger could be computed by comparing the amounts of each ion present (as determined by

the electrodes) with that to be expected based only on the known addition of salt(s), acid or base to the titration vessel. It is, in fact, a mass balance calculation, the capacity (mmol/g) for chloride ion (XCl) is given in Eq. [5.7], where Cl represents mmoles of chloride from each source.

$$XCl = (Cl_{added} + Cl_{initial} - Cl_{measured})/G \qquad \text{Eq.[5.7]}$$

Concentrations were obtained from ISE potential measurements by the methods outlined below. Consider the case of a chloride electrode with emf, E, a linear (Nernstian) response and known slope and E_o from its calibration (see Section 4.5). For a straight line calibration fit to the titration data a pCl value was calculated, Eq.[5.8].

$$pCl = (E - E_o)/slope \qquad \text{Eq.[5.8]}$$

In cases where a second order curve fit calibration was needed (see Section 4.5), a pCl value was assumed and using Eq. [5.8] as a first approximation an E value was calculated. This was repeated in an iterative cycle until the calculated potential was less than 0.01 mV different from the measured reading. The ion activity was then converted into the corresponding ion concentration by division with the activity coefficient. The activity coefficient was calculated from the ionic strength using the Davies (2) equation, Eq. [5.9].

$$\log \gamma = -0.5(\sqrt{I}/(1 + \sqrt{I}) - 0.3I) \qquad \text{Eq.[5.9]}$$

5.2.2 Computational System

The computational system used to process titration data of this thesis (see computer programs Appendix P4) begin with the calibration equation program (Appendix P4.2). In this program, the mV readings from the electrodes during their calibration are translated into a 'working' slope and E_o by a least squares method. The calibration data was curve fitted into both a first and second order polynomial. This resulted in two equations, Eq. [5.12] and [5.13].

$$E = A_o + A_1(pX) \qquad \text{Eq. [5.12]}$$

$$E = B_o + B_1(pX) + B_2(pX)^2 \qquad \text{Eq. [5.13]}$$

Eq. [5.12] is the best linear equation for the calibration data. A_o is a constant and A_1 is the slope of the line which will minimise the standard deviation of data errors off a straight line. Eq. [5.13] is the best curve fit equation. B_o is a constant and B_1 is the slope for the polynomial. B_2 is the curvature and its value helps assess whether the quadratic equation accounts for a significantly greater part of the variability. As seen in Tables 4.2 through 4.5, the best linear fit to the calibration data for many electrodes is sufficient for determining a 'working' slope and E_o.

Each electrode's slope and E_o, along with other experimental parameters, such as: grams of material used, molarities and volumes of the various reagents during a titration, were stored in Create2 program (Appendix P4.3).

The Uptake2 program, fully annotated in Appendix P4.4,

manipulates the data previously stored in the Create2 file. As explained in Sections 4.2 and 5.2.1, the mV readings from the ISEs are translated into corresponding activities through use of the Nernst equation (Eq. [4.3]) employing the calibrated 'working' slope and E_o. These activity values are changed into concentrations by dividing with an activity coefficient derived from the Davies equation (Eq. [4.7]) from the known ionic strength. These concentrations are used in the mass balance equation (Eq. [5.7]) to calculate 'uptake' or 'release' of a particular ion to or from the exchanger. Distribution coefficients are also calculated:

$$D_i = \overline{c_i} / c_i \qquad \text{Eq. [5.14]}$$

where $\overline{c_i}$ and c_i represent concentrations of the ion, i, on the exchanger (mmol/g) and in the external solution (mmol/ml), respectively. The capacities and distribution coefficients were calculated for each electrode in the titration system.

These results were tabulated using the Print Results program (Appendix P4.5) and graphically displayed on screen and 'screen dumped' by use of the Multiplot program given in Appendix P4.6. Many of the graphs presented in this thesis have been 'screen dumped' from the computer monitor screen on to paper using a dot matrix printer. These programs allow quick manipulation, tabulation, display and comparison of the titration data and results. All programs were written in Microsoft GWBASIC Version 3.2 on an Apricot Model F2 microcomputer.

5.3 Results and Discussion

5.3.1 Control Experiment

The method for determination of capacity from ISE data, discussed in the previous section, was employed for all electrodes used in this work. An experiment was devised to test the credibility of the electrodes and the capacity computations. The experiment intended to reproduce the typical combination of acid, base, and salts that are 'seen' by the electrodes during a normal βFeOOH potentiometric titration. Without the presence of βFeOOH ion exchange crystals there is no source or sink of added electrolyte. Therefore, we expect a null effect or zero uptake calculated for the hydrogen, chloride, and sodium electrodes monitored. This control experiment tests the ISEs response to typically occuring experimental parameters.

Typical data for a titration of βFeOOH, dispersed in water (20 ml), using sodium hydroxide as titrant, are given in Table 5.1. βFeOOH was prepared in the chloride form. On addition of water the pH was typically 3.5 due to release of HCl. The 'loaded' chloride ions in the pore come to equilibrium with the external solution rendering an external chloride activity of 10^{-3} M. Subsequent titration with sodium hydroxide progressively released chloride and protons until about pH 9 when no further chloride remains in the crystals (Eq.[5.10]).

$$\overline{FeOOH_2^+Cl^-} + NaOH = \overline{FeOOH} + NaCl + H_2O \qquad \text{Eq.[5.10]}$$

In this titration the activities of pH, pCl, pNa were determined with ISEs. The amounts of chloride and protons released after each addition of sodium hydroxide was obtained using Uptake2 computer program (Appendix P4.4). In this program the gain or loss of these ions in solution was computed by comparing the amounts of each ion present (as indicated by the electrodes) with that expected based on the additions of salt, acid or base to the titration vessel. It is, in effect, a mass balance calculation and is dependent upon the reliability of the electrodes, under proper standardisation, and the validity of activity corrections and other procedures incorporated in the computer program.

To test these procedures and the validity of the titration methods, a control titration was devised. This used, as closely as possible, the same initial conditions, solution volumes, reagents and electrodes as in the titration of a βFeOOH dispersion, as in Table 5.1. It was therefore decided upon use of a 10^{-3} M solution of hydrochloric acid at the start, thereby simulating the same chloride concentration at similar pH of the comparison βFeOOH experiment. The pH was adjusted to that of the corresponding point in the dispersion titration by addition of HCl from a burette. Thus a 'ghost' titration was created. As far as possible, the solution compositions were those of an actual titration. These data were processed with the standard uptake program (Appendix P4.7), just as original, but now, since the HCl additions are included, an exact mass balance between quantities of ions detected and

added should be obtained. The 'uptake' or 'release' should be zero, within the precision of the method. A result of zero uptake would establish good ISE behaviour and confirm data processing methods.

As can be seen in Table 5.2 and Figure 5.2 the null effect expected from hydrogen, chloride, and sodium electrodes was in fact obtained. The only discrepancy from a null effect was found for data obtained by the sodium electrode in the pH range 3-5.6. This may be attributed to hydrogen ion interference: at this stage of the titration such a small amount of sodium has been added, from base additions, that the sodium ISE responds to the hydrogen ion activity. This is well known behaviour by a glass sodium electrode since it resembles the glass hydrogen electrode in structure. Fortunately we are interested in sodium ion uptake in alkali where the electrode behaves satisfactorily. Table 5.2 shows excellent null effects for the chloride, hydrogen and sodium (above pH 5.6) electrodes.

The control experiment was identical to a titration with crystals present in all respects, including the additions of base, except that now the pH was adjusted to that of the corresponding point in the dispersion titration, by addition of HCl from a burette. The experiment, therefore, has two very important functions. Besides establishing an exact mass balance through ISE response, it also reproduces the release of chloride from the exchanger by means of a controlled known HCl solution addition by burette. This method mimics the crystalline

ion exchangers performance under such conditions. Therefore, the HCl burette becomes an analogue of the crystalline βFeOOH ion exchanger during titration and can be compared to results with the exchanger present.

In order to compare the control experiment with a βFeOOH titration some modifications must be made. These two titrations are not quite identical in all respects since there is an inevitable increase in volume due to HCl solution additions not parallelled in the 'real' βFeOOH titration. This volume and its associated change in ionic strength are accounted for in Eq.[5.11]. This equation is reproduced directly from the Null test computer program (Appendix P4.7). This program requires both sets of data, from the control and dispersion experiments, in order to take activity coefficients and volume effects into account, so that a direct comparison can be made.

$$XX = B - (V * \gamma T) / (VT * \gamma) * (BT-BT_i-AT) / G \quad \text{Eq.[5.11]}$$

In this equation, B, V, G and γ represent mmol base, total volume, grams exchanger and activity coefficient for the comparison titration with crystals present. VT and γT are total volume and activity coefficient in the control experiment where an inevitable increase in volume occured. (BT - BT_i - AT) is the balance of mmol base added minus the initial addition of base to get to the starting pH minus the acid added from the burette in the control experiment. Therefore, XX (which is capacity in mmol/g calculated from the HCl burette additions in the control) is a mass balance of mmoles of base added in the 'real' titration and

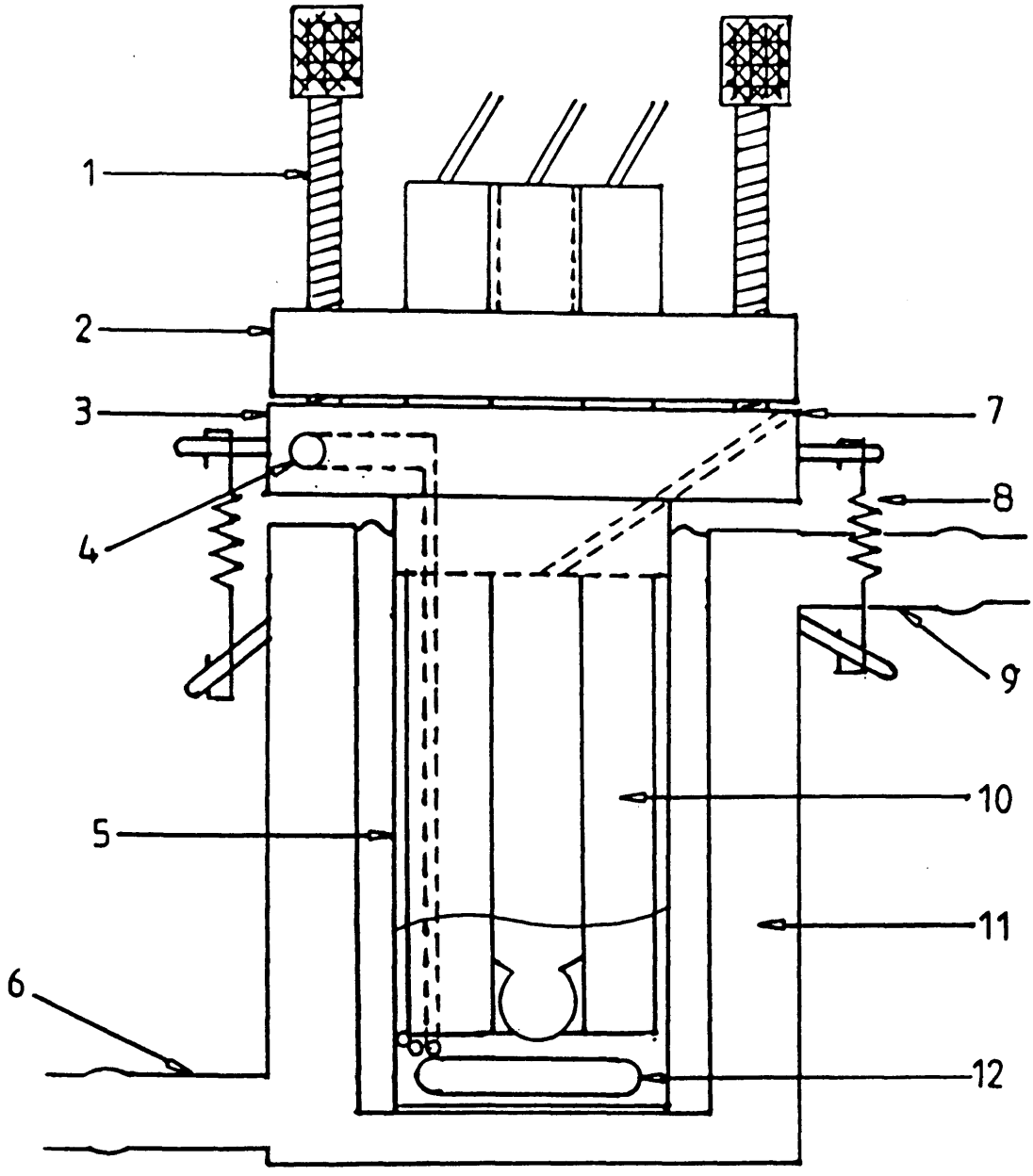
the base minus acid additions in the control multiplied by a factor that cancels out the volume and activity coefficient differences in the two titrations. In this way a true comparison can be made between capacity calculated from electrode mass balance when crystals are present versus capacity determined from burette additions.

This analogue of the crystalline behaviour requires that the release of chloride from βFeOOH, calculated in the 'real' experiment, will be equalled by the quantity of HCl added at the corresponding point in the control titration. The capacity values calculated from the HCl burette additions, XX computed by the Null test program, are shown in Table 5.2. This data can now be contrasted with uptake, X, computed by the Uptake2 program in the regular βFeOOH titration (Table 5.1). Good correlation is displayed for these relative capacities in Fig. 5.3.

Based on these results we infer that the chloride, hydrogen, and sodium electrodes are well-behaved under experimental conditions and the computer program for computation of uptake is believable because without ion exchange crystals present an exact mass balance is obtained (Fig. 5.2). Hydrogen ion interference to the sodium electrode below pH 6 was also disclosed defining further the practical limitations of the electrodes. Also, the 'ghost'capacity values determined by addition of hydrochloric acid via the burette macroscopically demonstrate release of HCl from the βFeOOH microcrystalline ion exchanger and bear semblance to real chloride capacities of this exchanger. The importance of the

control titration as a comprehensive test of the complete titration/computational methods cannot be overstressed.

FIGURE 5.1



1	Height Adjustment	7	Reagent Inlet Port
2	Electrode Holder	8	Spring
3	Cell Cap	9	Water Outlet
4	Nitrogen Inlet	10	Electrodes (Four)
5	Polypropylene Beaker	11	Double Wall Glass Beaker
6	Water Inlet	12	Stir Bar

TITRATION CELL

Table 5.1 βFeOOH Titration Data with added NaOH

NAME OF FILE =B786NA

Concentration of NaCl = 0.00 M Concentration of NaOH = 0.091 M

Concentration of HCl = 0.00 M Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of Acid, ml. VS = Volume of Salt, ml.

XNa = Na^+ Capacity in mmol/g XH = H^+ Capacity in mmol/g

XCl = Cl^- Capacity in mmol/g

N	VB	VA	VS	pH	XNa	XCl	XH
1	0.00	0.00	0.00	3.44	-0.297	0.000	0.000
2	0.10	0.00	0.00	3.82	-0.180	-0.030	-.014
3	0.20	0.00	0.00	4.17	-0.115	-0.052	-.037
4	0.30	0.00	0.00	4.57	-0.056	-0.088	-.062
5	0.40	0.00	0.00	4.92	-0.031	-0.127	-.090
6	0.50	0.00	0.00	5.27	-0.010	-0.171	-.117
7	0.60	0.00	0.00	5.56	-0.007	-0.210	-.145
8	0.70	0.00	0.00	5.84	0.001	-0.260	-.174
9	0.80	0.00	0.00	6.14	0.015	-0.307	-.202
10	0.90	0.00	0.00	6.44	0.020	-0.345	-.230
11	1.00	0.00	0.00	6.70	0.015	-0.389	-.258
12	1.10	0.00	0.00	6.93	0.011	-0.425	-.287
13	1.20	0.00	0.00	7.19	0.006	-0.463	-.315
14	1.30	0.00	0.00	7.49	-0.002	-0.493	-.343
15	1.40	0.00	0.00	7.85	-0.013	-0.524	-.371
16	1.50	0.00	0.00	8.22	-0.011	-0.566	-.400
17	1.60	0.00	0.00	8.50	-0.027	-0.588	-.428
18	1.70	0.00	0.00	9.43	-0.032	-0.606	-.454
19	1.80	0.00	0.00	10.42	-0.065	-0.577	-.464

Table 5.2 'Ghost' Titration Data with added NaOH and HCl

NAME OF FILE =T786NA

Concentration of NaCl = 0.00 M Concentration of NaOH = 0.106 M

Concentration of HCl = 0.01 M Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of Acid, ml. VS = Volume of Salt, ml.

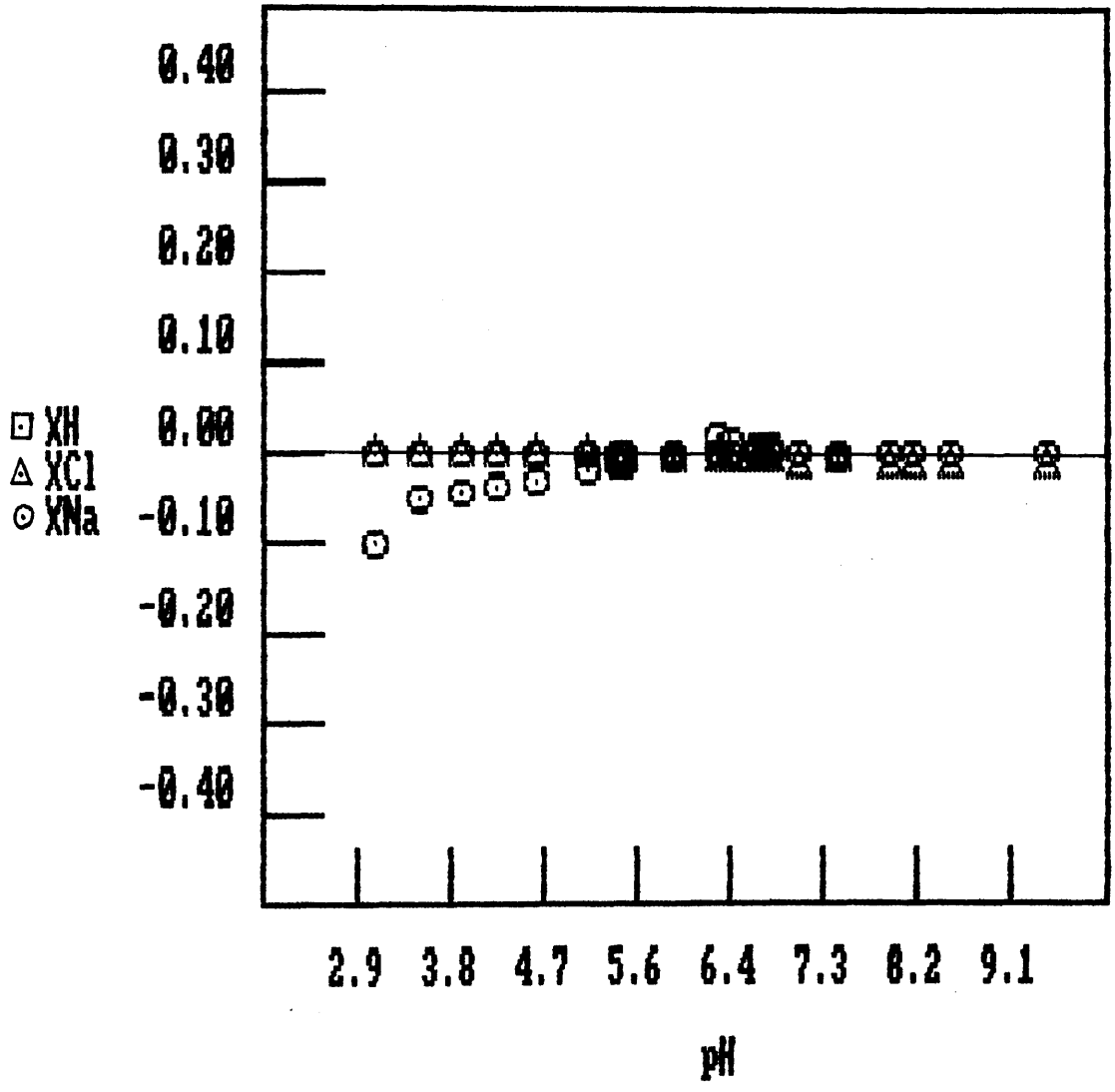
XNa = Na^+ Capacity in mmol/g XH = H^+ Capacity in mmol/g

XCl = Cl^- Capacity in mmol/g XX = HCl Burette Capacity

N	VB	VA	VS	pH	XNa	XCl	XH	XX
1	0.00	0.00	0.00	3.04	-0.102	0.000	0.000	0.000
2	0.12	0.00	0.00	3.47	-0.048	0.000	-.000	0.012
3	0.22	0.62	0.00	3.86	-0.042	-0.001	-.000	-.005
4	0.32	1.53	0.00	4.21	-0.040	-0.002	-.000	-.031
5	0.42	2.50	0.00	4.57	-0.033	-0.002	-.000	-.059
6	0.52	3.47	0.00	5.06	-0.019	-0.003	-.001	-.087
7	0.62	4.54	0.00	5.35	-0.013	-0.003	-.001	-.117
8	0.72	5.62	0.00	5.42	-0.013	-0.005	-.001	-.148
9	0.82	6.69	0.00	5.89	-0.003	-0.005	-.001	-.178
10	0.92	7.73	0.00	6.30	0.019	-0.007	-.001	-.207
11	1.02	8.83	0.00	6.44	0.015	-0.008	-.000	-.238
12	1.12	9.86	0.00	6.69	0.007	-0.008	-.001	-.267
13	1.22	10.90	0.00	6.83	0.004	-0.008	-.001	-.296
14	1.32	11.95	0.00	7.09	0.002	-0.009	-.001	-.325
15	1.42	12.98	0.00	7.47	-0.007	-0.008	-.001	-.354
16	1.52	13.97	0.00	7.96	0.001	-0.011	-.002	-.382
17	1.62	15.07	0.00	8.18	-0.000	-0.013	-.002	-.412
18	1.72	16.14	0.00	8.53	-0.000	-0.012	-.002	-.441
19	1.82	16.98	0.00	9.44	-0.002	-0.012	-.003	-.466

FIGURE 5.2

Test Titration for Zero Uptake from Hydrogen, Chloride and Sodium Electrodes versus pH



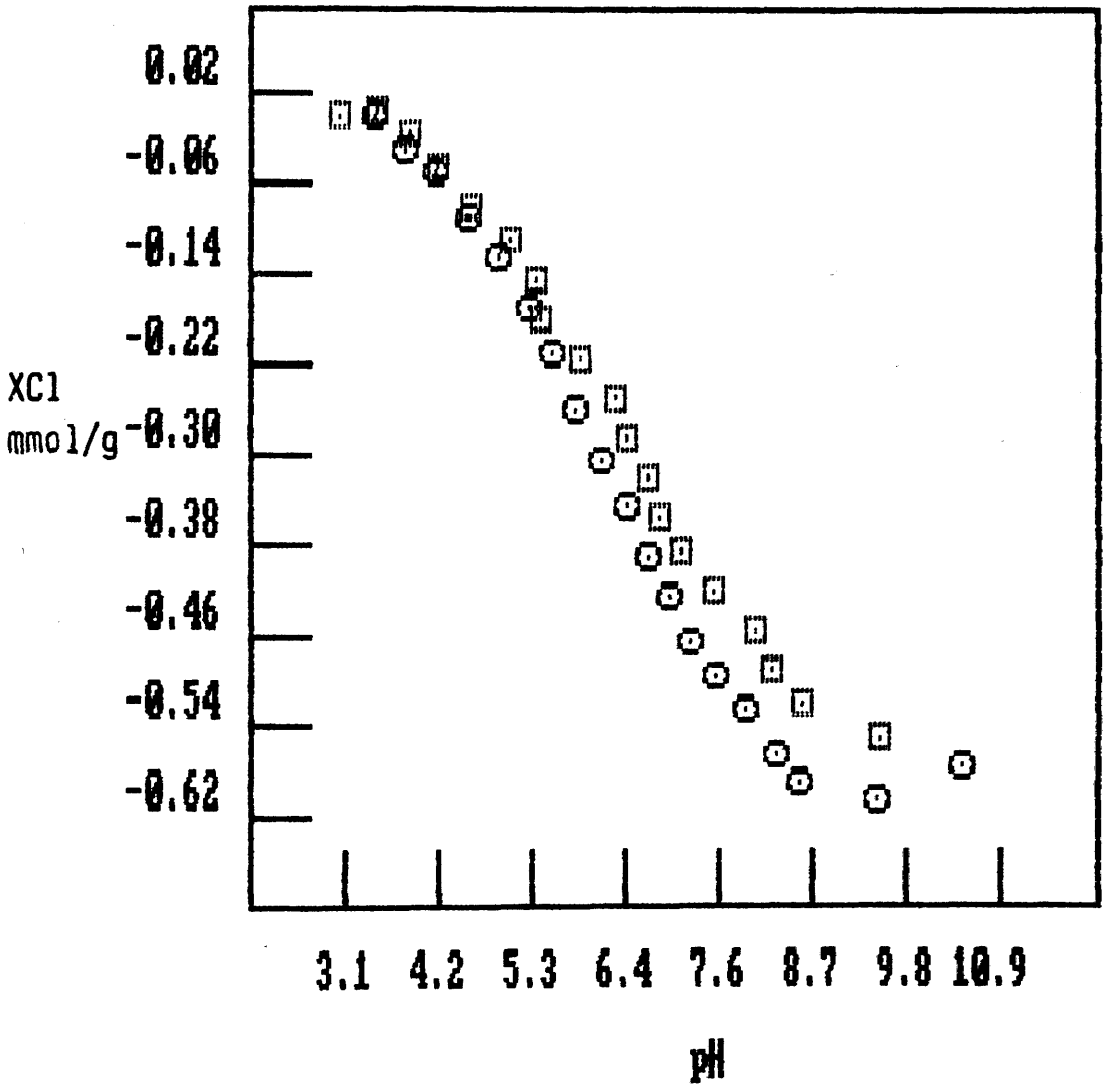
FILE 1 T786MA

FIGURE 5.3

Chloride Capacity vs. pH determined by two methods :

βFeOOH Titration with a Chloride Electrode and

HCl Burette Additions to a Test Solution



FILE 1 B786NA ⊙ XH TABLE 5.1
FILE 2 T786NA ⊡ XX TABLE 5.2

REFERENCES

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2. C.W.Davies, Electrochemistry, William Clowes and Sons, London (1967)

CHAPTER SIX

ION EXCHANGE PROPERTIES OF βFEOOH

Introduction

βFeOOH was first prepared by Bohm (1) and later the preparation, crystal structure and morphology was studied in detail in a series of papers by Mackay (2,3,4). It occurs in nature as the mineral akaganeite and can be prepared by synthetic methods. Hydrolysis of dilute ferric chloride; chloride being essential for the formation and stability of the beta form of the oxide-hydroxide, is the most common method. When prepared by such methods (Chapter 3), the βFeOOH is found to consist of cigar shaped crystals of 2000 Å in length and 400 Å wide square cross-section. X-ray powder diffraction studies (2) show the crystals to have the hollandite ($BaMn_8O_{16}$) structure, with a tetragonal unit cell (a = 10.48 Å and c = 3.02 Å) and space group I4/m. The small crystal pore, which in hollandite, contain barium ions, in βFeOOH contain chloride ion and water (2). In this work, through pH and ISE titration techniques, the chloride is extractable in a reversible manner. βFeOOH is shown to be a variable capacity anion exchanger with a maximum usable capacity of 0.6 mmol/g of air dried crystals.

The capacity for counterion chloride was not only pH dependent, but also equally dependent on the activity of chloride in the external solution phase. This observation is a consequence of the mechanism of exchange (see Chapter 2), which involves coupled participation of both proton and chloride adsorption. Chloride exchange capacity is a single-valued function of the activity of the whole acid (in this case HCl) in the external solution. It is

conveniently expressed as a function of 'pA', the negative logarithm of the acid activity, pA = pH + pCl.

Capacity data were originally obtained from pH titration (5). In this research, rigorous use of ion selective electrodes (see Chapter 4) and direct analysis confirm earlier conclusions and provide new methods for the determination of ion exchange characteristics on oxide hydroxides. βFeOOH is shown to exclude iodide and bromide, like perchlorate as shown previously (6), by an ion sieve mechanism from the 5 Å pores of its hollandite structure (7). It is also shown to take up fluoride in a more complex chemistry. Sodium ion is proved to be excluded from the exchanger. Since mineral hollandite ($BaMn_4O_{16}$) contains barium ion in its pores, the uptake of barium into the hollandite-type pores of βFeOOH was examined. Also, the uptake of calcium is much less, suggesting uptake by surface sites only.

6.1 Experimental

6.1.1 Flame Emission Spectroscopy

The barium and calcium uptake of βFeOOH was determined by flame emission spectroscopy utilising a Perkin Elmer model 370A instrument. The flame emission technique requires the flame to convert the aqueous sample into an atomic vapour and then thermally elevate the atoms to an excited electronic state. When these atoms return to the ground state, they emit light which is detected by the instrument. The intensity of light emitted is related to the concentration of the element of interest in solution by means of a calibration curve. The operating parameters for barium samples were at a fixed wavelength of 553.6 nm with a hollow cathode lamp and nitrous oxide-acetylene flame. The operating parameters for calcium analysis were at a fixed wavelength of 422.7 nm with a hollow cathode lamp light source and an air-acetylene flame.

Since maximum cation capacity is determined in alkaline pH, βFeOOH was dispersed with sodium hydroxide (sodium proven to be excluded from the pores) at pH 11. 1 mmol barium chloride or calcium chloride was added per gram of sample dispersed with water, under nitrogen, and mixed for fifteen minutes. Samples were withdrawn, filtered through a 0.22 μm Millipore filter and diluted by a factor of twenty to meet the optimum measuring range requirements of the Perkin Elmer instrument. 0 to 20 ppm standards for the calibration curve were made up with the same water and sodium hydroxide concentrations as the

samples. All calibration and sample solutions analysed had a background of 1000 ppm strontium to quench the effects of ionisation interference.

6.1.2 Gran Plot of Mixed Halides

A Gran plot method was used to confirm ISE results during a titration of βFeOOH with added halide salts. At various points during a titration, aliquots of the dispersion were drawn out with a syringe and filtered through a 0.22 μm Millipore filter to remove the iron oxide crystals. The filtrate was analysed, following the procedure given in Appendix C4.3, by silver nitrate titration. These results are read into the Gran plot program (Appendix P4.1) where they are converted into halide concentration before the endpoint and silver ion concentration after the endpoint.

6.2 Results and Discussion

A number of titrations were made on different samples of βFeOOH with alkali and typical titration curves are shown in Fig. 6.1. In that figure there appear two distinct titration plots, which merge in alkaline solution above pH 10. The lower curve was obtained when βFeOOH was dispersed in water and titrated with sodium hydroxide, with no added sodium chloride present. The pH curve rises steeply from pH 3 to 9 and gives finally an indistinct end point unsuitable for quantitative determinations. Titration data are given in Table 6.1. If the same standard sample of air dried βFeOOH (0.3007 g) was again dispersed in 20 ml of water and now 1 mmol of sodium chloride is added, the pH of the suspension rose by over one pH unit, Table 6.2, Fig. 6.1. Thereafter on addition of base, the pH followed the upper curve to the end point. This transition could be made at any point by addition of sodium chloride.

Dispersions of βFeOOH in water gave a pH of approximately 3.5. Salt addition in acidic solutions caused proton uptake by the exchanger (see Section 2.3). This is a very sensitive test of uptake, since a large pH change, say between pH 4.9 to pH 6.1 (Fig. 6.1), due to the displacement of the equilibrium (Eq. [2.10]), would amount to a chloride uptake of solution into the solid of 2×10^{-7} moles.

A more exact account of the acid/base balance between solution and βFeOOH is obtained by the calculation of ΔX (Eq. [5.1]) and defined in theory as the release of acid

(mmol/g FeOOH), during the titration, taken relative to the initial capacity of the βFeOOH sample dispersed in water. ΔX values for the titrations given in Fig. 6.1 were calculated from chloride ion selective electrode mass balance (Eq. [5.7]) and are given in Tables 6.1 and 6.2. Plots of the absolute capacity against pH for these titrations are given in Fig. 6.2. All points fall on two curves. Transition between them, made by the addition of salt at intermediate stages are indicated by arrows. Fig. 6.2 shows that sodium chloride addition increases pH, indicating that βFeOOH has a larger capacity for acid at any given pH if additional chloride is present. Therefore, capacity is not a single-valued function of pH, but depends strongly on chloride concentration in the equilibrium solution. This is graphically represented in Fig. 6.3 when the same data are plotted as a function of pH + pCl they combine to a single curve. In the titrations of βFeOOH the proton release monitored by the pH electrode was shown to be accompanied always by a stoichiometric amount of chloride release monitored by the chloride ISE.

6.2.1 Iodide and Bromide Rejection by an Ion Sieve Mechanism

The first substantiated case of an anion sieve, was the exclusion of perchlorate ion from the pore sites in βFeOOH proved by Paterson and Rahman (6). Unlike chloride ion, perchlorate did not cause an increase in pH and therefore was not involved in an analogous equilibrium to Eq. [2.10]. In this work it was observed that additions of iodide and bromide caused little or no increase in pH of βFeOOH dispersions in water under conditions where equimolar additions of chloride gave pH rises of greater than one unit. Subsequent filtration and analysis of the iodide and bromide solutions in equilibrium with βFeOOH showed no loss of these halide ions to the exchanger (see Section 6.2.2). There is, therefore, good evidence that bromide and iodide ions are also excluded from the pores by an ion sieve mechanism, as shown for perchlorate previously (6).

Titrations of the chloride form of βFeOOH were made using sodium hydroxide. Aliquots of sodium iodide or sodium bromide were added in the acid range. A comparison of pH titrations with added chloride, perchlorate, iodide and bromide is given in Fig. 6.4. The lower curve represents the salt-free titration of a single crystal dispersion of βFeOOH. Once again the upper curve represents the large pH shift that is observed when 1 mmol chloride salt is added at pH 4.9. The titrations obtained for added perchlorate, iodide and bromide all fall upon the lower

pH when 1 mmol (1ml x 1M) sodium perchlorate, sodium iodide or sodium bromide are added, respectively. This is strong circumstantial evidence that these ions are not involved in equilibria with pore sites in the hollandite structure of βFeOOH.

Calculations showed also that the total capacity, ΔX, of the exchanger remained unaffected by iodide and bromide additions and remained a single-valued function of the activity of hydrogen and chloride alone. This is displayed in Fig. 6.5 where each chloride capacity in the presence of added iodide, bromide or perchlorate all fall upon the the same curve.

Equilibrations at constant pH were made between 0.3 g samples of βFeOOH and 10 ml aliquots of iodide or bromide of increasing concentration in the 10^{-3} to 10^{-2} M range. These additions were made in 1 ml increments and the iodide and bromide activities were followed using ion selective electrodes. These results are shown in Table 6.6 together with the direct analysis results by silver nitrate Gran plot treatment of filtered samples.

6.2.2 Gran Plot Results for βFeOOH Iodide and Bromide Equilibrations

In addition to determination using ISEs, the solutions of Section 6.2.1 were filtered and analysed directly for iodide, bromide and chloride by potentiometric titration using silver nitrate (see Section 6.1.2). The titration curve for a typical 'mixed' halide filtrate, that is a

solution with both chloride and iodide present, is shown in Fig. 6.6. It is apparent that the silver nitrate method can distinguish between the two ions as there are two distinct endpoints. Emf data were examined using a Gran plot method (8) modified to include activity and solubility corrections (see computer program given in Appendix P4.1). An elegant feature of this program is that the activity of the silver or halide ion due to the solubility of the silver halide precipitate is accounted for in the total halide or silver concentration calculated. These values are plotted against ml titrant in Fig. 6.7 which results in two straight lines which intersect at the endpoint. These results along with the ISE determinations are shown in Table 6.6. Excellent agreement was obtained between halide concentrations determined using ISEs and those obtained by direct analysis. Neither iodide nor bromide is taken up in an equilibrium dispersion of βFeOOH from pH 3.6 to 11.6 within experimental error. The amount of iodide or bromide measured by the ISE or the silver nitrate titration is within $\pm$5 % of the quantity of the iodide or bromide salt added. When selectivity coefficients for chloride ion over iodide or bromide ion are calculated (9), the minimum molar selectivity coefficient $K \approx 303$. We estimate therefore that βFeOOH is more than 300 times more selective for chloride than for iodide or bromide.

6.2.3 ISE Determination of Fluoride Uptake in βFeOOH

Fluoride ion exchange in zirconium oxide hydroxide crystals was studied by Thomae (10) in a manner similar to techniques used here (see Section 7.3.2). Since the fluoride ion selective electrode was reliable (11) experiments were designed to follow the ion exchange of fluoride on βFeOOH crystals.

The typical titration was performed on a dispersion of 0.3 g of βFeOOH in the chloride form in 20 ml water. Hydrogen, chloride and fluoride electrodes were used. Initially, the system, at pH 3.5, was titrated forward with sodium hydroxide to pH 11, thereby removing all chloride from the pores of the exchanger. At this stage 0.4 mmol sodium fluoride was added and the system was backtitrated to pH 5 using perchloric acid. Table 6.7 shows the results from this experiment. Fluoride capacity was 0.331 mmol/g at pH 5.6. Once the chloride was removed from the hollandite pores of βFeOOH and the fluoride was added, the chloride does not reenter the pores (see Fig. 6.8) as would be expected if fluoride were not present, shown by reversibility studies previously (12).

When the experiment was repeated at pH 7 rather than pH 5 there was 50% less uptake of fluoride. Distribution coefficients (defined as the ratio of the concentration of fluoride in the exchanger (mmol/g) to the concentration of fluoride in the external solution (mmol/ml)) were plotted against pH + pF in Figure 6.9. The distribution coefficient is 0.913 at pH 5 and 0.467 at pH 7.

Perchloric acid was used as the backtitrating acid in

these experiments as it was established previously (6) that the perchlorate anion will not enter the hollandite pores of βFeOOH. If the backtitrating acid were to be hydrochloric acid, (exchangeable) chloride ion would have been introduced progressively in the presence of fluoride. The titration data for this case are given in Table 6.8. In this instance both chloride and fluoride ions were taken up. There was a maximum observed ≈ 0.3 mmol/g uptake of chloride and ≈ 0.3 mmol/g uptake of fluoride ion at pH 4.5. Total anion capacity (XCl + XF) for this titration may be compared with the chloride capacity (XCl) alone from a previous experiment, in which fluoride was absent. The results are given in Fig. 6.10 where both are plotted versus pH + pCl. The fluoride and chloride capacities are additive to a constant value, previously determined by chloride alone, of about 0.6 meq/g.

The importance of chloride ion in the production of synthetic βFeOOH was noted by Ellis, et al. (13) and others. Chloride ion stabilises the crystal lattice and cannot be fully eluted by washing with water or inert anions to less than 2%. This result was also shown by Dousma, et al. (14). These findings are upheld by the results shown in this research (Section 6.2.1 and 6.2.2) by the exclusion of iodide and bromide from these crystals. The results in this section show clearly that fluoride is taken up by βFeOOH and since the total capacity (XCl + XF) is similar to that of chloride alone at the same pH, it appears that fluoride may enter the hollandite pores and replace chloride.

Investigation of literature sources showed that the beta form of the iron oxide hydroxide could only be synthesised in the presence of chloride or fluoride (15). This suggested the possibility of preparing βFeOOH microcrystals from ferric fluoride. As reported in Chapter 3, the method of Childs, et al. (16) using the Mossbauer spectra technique analysed βFeOOH prepared in the presence of chloride and fluoride ions. They report the hyperfine structure of βFeOOH pores to be 3.5 Å diameter in the cavity and 2.7 Å diameter at the necks of the cavities. It is of interest to note that the diameter of chloride is 3.6 Å, almost identical with that estimated for the size of each cavity in the tunnels, whereas the 2.7 Å diameter for fluoride is somewhat smaller. There must be some error in the interpretation of the Mossbauer spectra, as the postulated 2.7 Å diameter of the neck would not let chloride ion enter the pore. At 295 K the spectra consist of overlapping paramagnetic doublets which indicate that there are two non-equivalent iron sites for exchange. Ohyabu and Ujihira (15), also using Mossbauer spectroscopy, report the requirement of the presence of fluoride or chloride in order to produce βFeOOH. Their analysis revealed that βFeOOH preferentially incorporated fluoride ions more than chloride ions. They suggest that chloride can occupy only one site in the crystal, but fluoride can occupy two different sites. Just as the observation that the beta form would not be formed from ferric iodide or bromide (17) provided valuable circumstantial evidence that iodide and bromide would be excluded (see Section 6.2.1), literature sources suggested fluoride would be taken up by

βFeOOH. This hypothesis was verified in this work. An assessment of possible mechanistic scenarios of fluoride exchange and adsorption is given in Section 7.3.2. Titrational investigation of βFeOOH prepared from ferric fluoride should help answer questions on its ion exchange capacity and whether or not there is isomorphous replacement of fluoride in the crystal lattice. Although, the case for βFeOOH may prove to be quite different from that of monoclinic zirconia.

In summary, fluoride is taken up by βFeOOH to a maximum capacity of 0.331 mmol/g at pH 5.6. Fluoride ion is preferred over chloride by the exchanger, but if the two ions are added concurrently uptake of both will occur.

6.2.4 Exclusion of Sodium Ion in Alkaline Solutions

An experiment was designed in order to test the past conclusion that βFeOOH does not exchange cations in alkali. Since sodium was the cation salt most widely used and a sodium ISE was available, a test was devised to determine whether sodium is picked up at all in alkali.

The conventional pH titration was performed, that is, dispersing 0.3 g βFeOOH in 20 ml distilled water and titrating with sodium hydroxide. This time both chloride and sodium were tracked with ISE's. The previous control experiment, Section 5.3.1, Fig. 5.1, had highlighted the likelihood of hydrogen ion interference on the sodium electrode in acidic pH. As a result, this electrode was trusted only above pH 6.

Typical titration data are given in Table 6.9. Eq. [5.19] is the mass balance equation used to calculate capacity for sodium uptake based on sodium hydroxide and sodium salts added minus the electrode measurement made for sodium. This equation is used in the standard sodium uptake computer program, listed in Appendix P4.8.

$$XNa = (B + S1 + S2) - C3M \;/\; G \qquad \text{Eq.[5.19]}$$

In this equation, XNa, sodium ion capacity in mmol/g, is calculated as a mass balance of sodium added to the dispersion, in the form of mmol base (B), mmol salt1 (S1) and mmol salt2 (S2), minus mmol sodium (C3M) determined by the sodium ISE in the external solution. As can be seen in Table 6.9 and Fig. 6.11, the sodium capacity, calculated

via mass balance, is zero. Fig. 6.11 shows a comparison of XCl (chloride capacity in mmol/g) and XNa (sodium capacity in mmol/g) versus pH + pCl. Chloride capacity is unchanged at 0.57 mmol/g and sodium capacity is zero.

These experiments verify the assumption, made in all βFeOOH potentiometric titrations thus far, that is that sodium ion is excluded from the ion exchange pores. Perhaps more importantly it established the power of this new methodology employing ion selective electrodes.

6.2.5 Cation Capacity by Flame Emission Spectroscopy

Since hollandite contains barium ion in its pores (18), barium uptake by the 5 Å hollandite-type pores of βFeOOH seemed the logical cation to study next. βFeOOH capacity for barium and calcium were analysed in alkaline pH according to the experimental design laid out in Section 6.1.1.

The capacity for barium was found to be 0.57 meq/g at pH 11. This is similar to the chloride capacity in the same βFeOOH crystals at pH 3. This suggests that the barium ion undergoes the same mechanistic ion exchange process as the chloride ion except performed as cation exchange at alkaline pH.

The capacity for calcium was determined by flame emission spectroscopy to be 0.24 meq/g at pH 11. This suggests a different mechanism of exchange. Possibly the calcium undergoes only surface site exchange, one of the two non-equivalent iron sites.

Table 6.1 βFeOOH Titration Data with no added Chloride Salt

NAME OF FILE =B886UP

Concentration of NaCl = 0.01 M Concentration of NaOH = 0.106 M

Concentration of HCl = 0.10 M Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of acid, ml. VS = Volume of salt, ml.

XH = H^+ Capacity in mmol/g

N	VB	VA	VS	pH	ΔXH	pA
1	0.00	0.00	0.00	3.450	0.000	6.900
2	0.20	0.00	0.00	4.156	-0.049	7.120
3	0.40	0.00	0.00	4.956	-0.113	7.655
4	0.60	0.00	0.00	5.587	-0.180	8.121
5	0.80	0.00	0.00	6.191	-0.247	8.608
6	1.00	0.00	0.00	6.606	-0.315	8.933
7	1.20	0.00	0.00	7.055	-0.382	9.310
8	1.40	0.00	0.00	7.531	-0.450	9.726
9	1.60	0.00	0.00	8.309	-0.517	10.452
10	1.80	0.00	0.00	10.127	-0.575	12.225
11	2.00	0.00	0.00	11.014	-0.572	13.074

ΔXH = Capacity relative to the initial condition

The absolute capacity is (ΔXH + 0.573)

Table 6.2 βFeOOH Titration Data with added Sodium Chloride

NAME OF FILE =B1185CL

Concentration of NaCl = 0.00 M Concentration of NaOH = 0.105 M

Concentration of HCl = 0.00 M Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of acid, ml. VS = Volume of salt, ml.

XH = H^+ Capacity in mmol/g

N	VB	VA	VS	pH	Δ XH	pA
1	0.00	0.00	0.00	3.488	0.000	6.975
2	0.20	0.00	0.00	4.130	-0.056	7.098
3	0.40	0.00	0.00	4.858	-0.126	7.563
4	0.40	0.00	0.00	6.055	-0.125	7.450
5	0.60	0.00	0.00	6.590	-0.199	7.981
6	0.80	0.00	0.00	7.114	-0.273	8.502
7	1.00	0.00	0.00	7.530	-0.348	8.913
8	1.20	0.00	0.00	7.962	-0.422	9.341
9	1.40	0.00	0.00	8.487	-0.496	9.862
10	1.60	0.00	0.00	9.080	-0.569	10.451
11	1.80	0.00	0.00	10.702	-0.595	12.070
12	2.00	0.00	0.00	11.095	-0.595	12.460
13	2.20	0.00	0.00	11.305	-0.590	12.668
14	2.40	0.00	0.00	11.445	-0.585	12.805
15	2.60	0.00	0.00	11.548	-0.580	12.905
16	2.80	0.00	0.00	11.632	-0.573	12.986
17	3.00	0.00	0.00	11.702	-0.565	13.053

Δ XH = Capacity relative to the initial condition

The absolute capacity is (ΔXH + 0.582)

Table 6.3 βFeOOH Titration Data with added Sodium Perchlorate

NAME OF FILE =B1185CLO

Concentration of NaClO4= 1.00 M Concentration of NaOH = 0.105 M

Concentration of HCl = 0.00 M Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of acid, ml. VS = Volume of salt, ml.

XH = H^+ Capacity in mmol/g

N	VB	VA	VS	pH	ΔXH	pA
1	0.00	0.00	0.00	3.451	0.000	6.903
2	0.20	0.00	0.00	4.072	-0.058	7.036
3	0.40	0.00	0.00	4.852	-0.130	7.556
4	0.40	0.00	1.00	4.852	-0.130	7.638
5	0.60	0.00	1.00	5.476	-0.207	8.094
6	0.80	0.00	1.00	6.121	-0.285	8.619
7	1.00	0.00	1.00	6.708	-0.363	9.114
8	1.20	0.00	1.00	7.263	-0.441	9.593
9	1.40	0.00	1.00	7.877	-0.519	10.145
10	1.80	0.00	1.00	10.805	-0.609	12.972
11	2.00	0.00	1.00	11.146	-0.607	13.272
12	2.20	0.00	1.00	11.335	-0.603	13.424
13	2.40	0.00	1.00	11.467	-0.597	13.523
14	2.60	0.00	1.00	11.567	-0.591	13.592
15	2.80	0.00	1.00	11.644	-0.587	13.641
16	3.00	0.00	1.00	11.711	-0.580	13.683

ΔXH = Capacity relative to the initial condition

The absolute capacity is (ΔXH + 0.589)

Table 6.4 βFeOOH Titration Data with added Sodium Iodide

NAME OF FILE =B1185I

Concentration of NaI = 1.00 M Concentration of NaOH = 0.105 M

Concentration of HCl = 0.00 M Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of acid, ml. VS = Volume of salt, ml.

XH = H^+ Capacity in mmol/g

N	VB	VA	VS	pH	ΔXH	pA
1	0.00	0.00	0.00	3.445	0.000	6.889
2	0.20	0.00	0.00	4.130	-0.051	7.098
3	0.40	0.00	0.00	4.887	-0.118	7.592
4	0.40	0.00	1.00	4.918	-0.118	7.705
5	0.60	0.00	1.00	5.572	-0.189	8.190
6	0.80	0.00	1.00	6.127	-0.259	8.624
7	1.00	0.00	1.00	6.636	-0.330	9.041
8	1.20	0.00	1.00	7.249	-0.401	9.579
9	1.40	0.00	1.00	7.709	-0.472	9.976
10	1.60	0.00	1.00	8.394	-0.543	10.608
11	1.80	0.00	1.00	10.636	-0.574	12.803
12	2.00	0.00	1.00	11.100	-0.566	13.226
13	2.20	0.00	1.00	11.322	-0.556	13.410
14	2.40	0.00	1.00	11.467	-0.544	13.522
15	2.60	0.00	1.00	11.565	-0.539	13.590
16	2.80	0.00	1.00	11.650	-0.528	13.647
17	3.00	0.00	1.00	11.720	-0.516	13.692

ΔXH = Capacity relative to the initial condition

The absolute capacity is (ΔXH + 0.576)

Table 6.5 βFeOOH Titration Data with added Sodium Bromide

NAME OF FILE =B1185BR

Concentration of NaBr = 1.00 M Concentration of NaOH = 0.105 M

Concentration of HCl = 0.00 M Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of acid, ml. VS = Volume of salt, ml.

XH = H^+ Capacity in mmol/g

N	VB	VA	VS	pH	ΔXH	pA
1	0.00	0.00	0.00	3.502	0.000	7.004
2	0.20	0.00	0.00	4.148	-0.059	7.117
3	0.40	0.00	0.00	4.937	-0.132	7.642
4	0.40	0.00	1.00	5.055	-0.131	7.843
5	0.60	0.00	1.00	5.684	-0.208	8.302
6	0.80	0.00	1.00	6.284	-0.285	8.781
7	1.00	0.00	1.00	6.939	-0.362	9.344
8	1.20	0.00	1.00	7.528	-0.439	9.858
9	1.40	0.00	1.00	8.265	-0.516	10.533
10	1.60	0.00	1.00	10.490	-0.562	12.704
11	1.80	0.00	1.00	11.021	-0.563	13.188
12	2.00	0.00	1.00	11.236	-0.570	13.361
13	2.20	0.00	1.00	11.390	-0.569	13.479
14	2.40	0.00	1.00	11.501	-0.568	13.557
15	2.60	0.00	1.00	11.587	-0.568	13.612
16	2.80	0.00	1.00	11.655	-0.570	13.653
17	3.00	0.00	1.00	11.717	-0.568	13.689

ΔXH = Capacity relative to the initial condition

The absolute capacity is (ΔXH + 0.569)

TABLE 6.6

EQUILIBRATIONS BETWEEN THE CHLORIDE FORM OF βFeOOH CRYSTALS AND SODIUM IODIDE OR SODIUM BROMIDE SOLUTIONS DETERMINED BY ISE AND DIRECT ANALYSIS

Initial Condition			Equilibrium Data		
			ISE Data	Direct Analysis with $AgNO_3$	
[NaI] added	[NaBr] added	pH	[NaI]/[NaBr]	[NaI]/[NaBr]	[NaCl]
0.0329		3.64	0.0329	0.0329	0.0012
	0.0325	3.66	0.0343	0.0335	0.0009
0.0329		11.61	0.0317	0.0319	0.0010
	0.0318	11.79	0.0327	0.0321	0.0007

Table 6.7 βFeOOH Titration with pH Cl and F Electrodes

NAME OF FILE =B1086F

Concentration of NaCl = 0.255 M Concentration of NaOH = 0.104 M

Concentration of HClO4= 0.095 M Concentration of NaF 0.010 M

Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of acid, ml. VS1 = Volume of chloride salt, ml.

VS2 = Volume of fluoride salt, ml.

XH = H^+ Capacity in mmol/g XCl = Cl^- Capacity in mmol/g

XF = F^- Capacity in mmol/g

N	VB	VA	VS1	VS2	pH	ΔXH	ΔXCl	XF
1	1.60	0.00	0.00	0.000	10.703	-0.590	0.000	0.000
2	1.60	0.20	0.00	0.000	9.828	-0.556	-0.012	-0.000
3	1.60	0.40	0.00	1.280	8.316	-0.484	-0.026	0.048
4	1.60	0.60	0.00	3.870	7.575	-0.405	-0.030	0.148
5	1.60	0.80	0.00	6.260	6.436	-0.327	-0.035	0.240
6	1.60	1.00	0.00	8.620	5.563	-0.248	-0.051	0.331
7	1.60	1.00	1.00	8.620	5.585	-0.248	-0.028	0.331
8	1.70	1.00	1.00	8.620	6.653	-0.291	-0.033	0.324
9	1.80	1.00	1.00	8.620	7.917	-0.334	-0.038	0.318
10	2.00	1.00	1.00	8.620	10.164	-0.399	0.038	0.318

ΔXH and ΔXCl = Capacity relative to the initial condition

The absolute capacity is (ΔXH + 0.590)

Table 6.8 βFeOOH Titration with Cl and F added Concurrently

NAME OF FILE =B886F

Concentration of NaCl = 0.000 M Concentration of NaOH = 0.106 M

Concentration of HCl = 0.100 M Concentration of NaF 0.010 M

Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of acid, ml. VS1 = Volume of chloride salt, ml.

VS2 = Volume of fluoride salt, ml.

XH = H^+ Absolute capacity,mmol/g

XCl = Cl^- Absolute capacity,mmol/g

XF = F^- Absolute capacity,mmol/g

N	VB	VA	VS1	VS2	pH	XH	XCl	XF
1	2.00	0.00	0.00	0.000	10.672	0.600	0.000	0.000
2	2.00	0.20	0.00	0.000	9.865	0.568	0.021	-0.001
3	2.00	0.20	0.00	0.100	9.923	0.567	0.024	0.002
4	2.00	0.40	0.00	1.500	8.777	0.510	0.058	0.042
5	2.00	0.60	0.00	3.600	7.485	0.447	0.076	0.103
6	2.00	0.80	0.00	6.000	6.512	0.384	0.097	0.173
7	2.00	1.00	0.00	8.100	6.021	0.320	0.139	0.233
8	2.00	1.20	0.00	10.200	5.338	0.257	0.196	0.294
9	2.00	1.40	0.00	12.500	4.443	0.198	0.253	0.360
10	2.00	1.60	0.00	15.000	4.134	0.140	0.300	0.432

Table 6.9 βFeOOH Titration Data with Chloride and Sodium ISEs

NAME OF FILE =B786NA

Concentration of NaCl = 0.00 M Concentration of NaOH = 0.091 M

Concentration of HCl = 0.00 M Initial Volume = 20.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of acid, ml. VS = Volume of salt, ml.

XNa = Na^+ Capacity in mmol/g XH = H^+ Capacity in mmol/g

XCl = Cl^- Capacity in mmol/g

N	VB	VA	VS	pH	XNa	ΔXCl	ΔXH
1	0.00	0.00	0.00	3.44	-0.297	0.000	0.000
2	0.10	0.00	0.00	3.82	-0.180	-0.030	-.014
3	0.20	0.00	0.00	4.17	-0.115	-0.052	-.037
4	0.30	0.00	0.00	4.57	-0.056	-0.088	-.062
5	0.40	0.00	0.00	4.92	-0.031	-0.127	-.090
6	0.50	0.00	0.00	5.27	-0.010	-0.171	-.117
7	0.60	0.00	0.00	5.56	-0.007	-0.210	-.145
8	0.70	0.00	0.00	5.84	0.001	-0.260	-.174
9	0.80	0.00	0.00	6.14	0.015	-0.307	-.202
10	0.90	0.00	0.00	6.44	0.020	-0.345	-.230
11	1.00	0.00	0.00	6.70	0.015	-0.389	-.258
12	1.10	0.00	0.00	6.93	0.011	-0.425	-.287
13	1.20	0.00	0.00	7.19	0.006	-0.463	-.315
14	1.30	0.00	0.00	7.49	-0.002	-0.493	-.343
15	1.40	0.00	0.00	7.85	-0.013	-0.524	-.371
16	1.50	0.00	0.00	8.22	-0.011	-0.566	-.400
17	1.60	0.00	0.00	8.50	-0.027	-0.588	-.428
18	1.70	0.00	0.00	9.43	-0.032	-0.606	-.454
19	1.80	0.00	0.00	10.42	-0.065	-0.577	-.464

ΔXH and ΔXCl = Capacity relative to the initial condition

The absolute capacity is (ΔXCl + 0.584)

FIGURE LEGENDS FOR CHAPTER SIX

Fig. 6.1 pH titration of βFeOOH with and without added sodium chloride (Tables 6.1 and 6.2). An equilibrium dispersion of 0.3007g of air-dried crystals (containing 0.2749g of FeOOH) in 20 ml water at 25 °C was titrated with 0.1050 M sodium hydroxide. The lower curve was obtained when no salt was added during the titration. The upper curve was obtained when 1 ml of 1.003 M sodium chloride was added after addition of 0.04 ml of base.

Fig. 6.2 Absolute chloride capacity (mmol/g) versus pH is plotted for data in Tables 6.1 and 6.2. Transition is made, between the two curves, by the addition of sodium chloride as described in legend Fig. 6.1.

Fig. 6.3 Chloride capacities from Table 6.1 and 6.2 plotted against pH + pCl, showing that XCl is a single-valued function of pH + pCl.

Fig. 6.4 pH titration of βFeOOH with added salts. 1 ml of 1 M sodium chloride added, as in legend Fig. 6.1, gave a large pH shift. Similar additions of sodium iodide (Table 6.4), sodium bromide (Table 6.5) and sodium perchlorate (Table 6.3) all fall on the lower curve.

Fig. 6.5 Chloride capacity (mmol/g) against pH + pCl. Additions of salts, as in legend Fig. 6.4, to raise the concentration of anion in solution to 0.1 M (as in Fig. 6.1) had no influence on the total chloride capacity or its dependence upon the chloride and hydrogen activities.

FIGURE 6.1

pH vs. ml NaOH with and without added Chloride

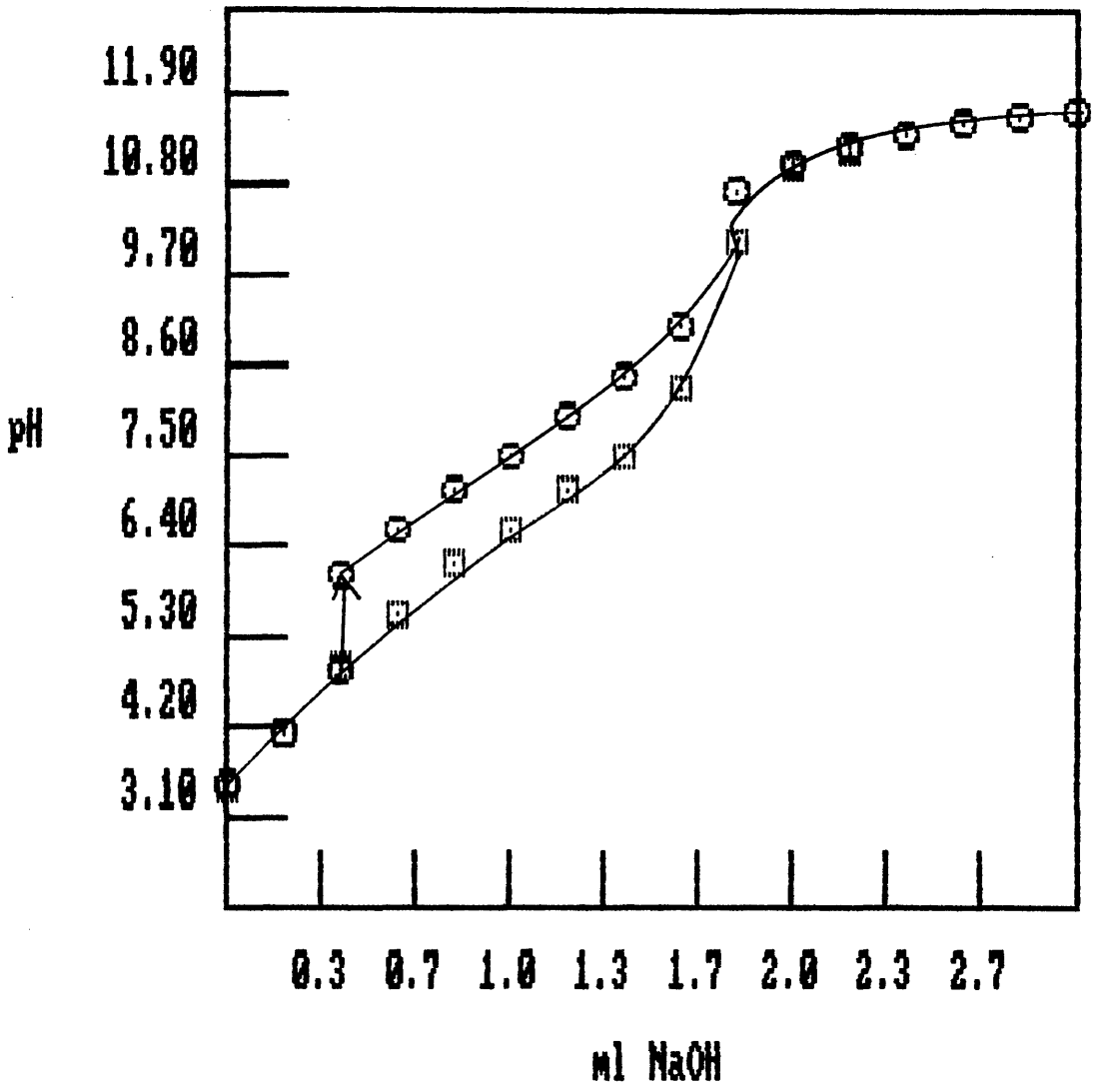
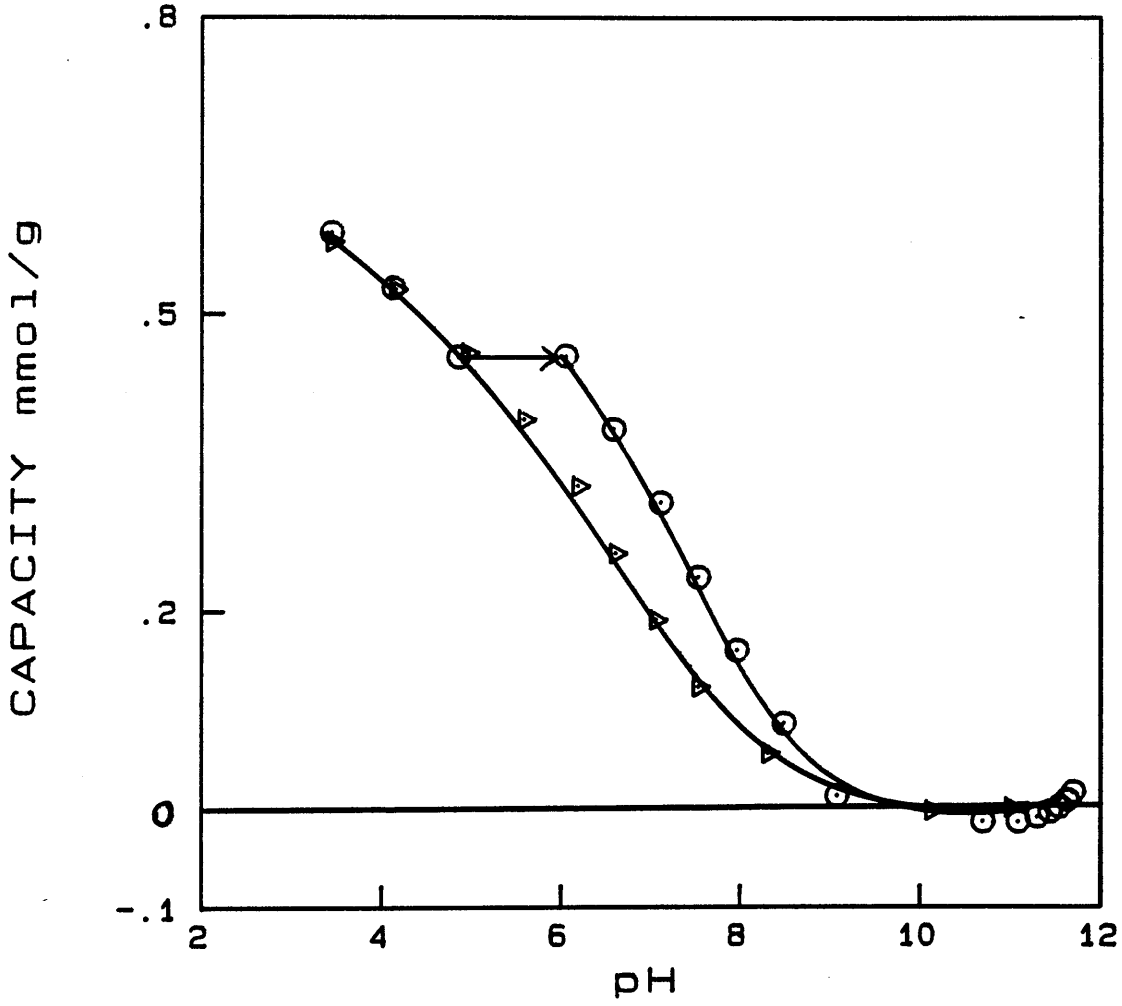


FIGURE 6.2

CHLORIDE CAPACITY VS pH

WITH AND WITHOUT ADDED NaCl

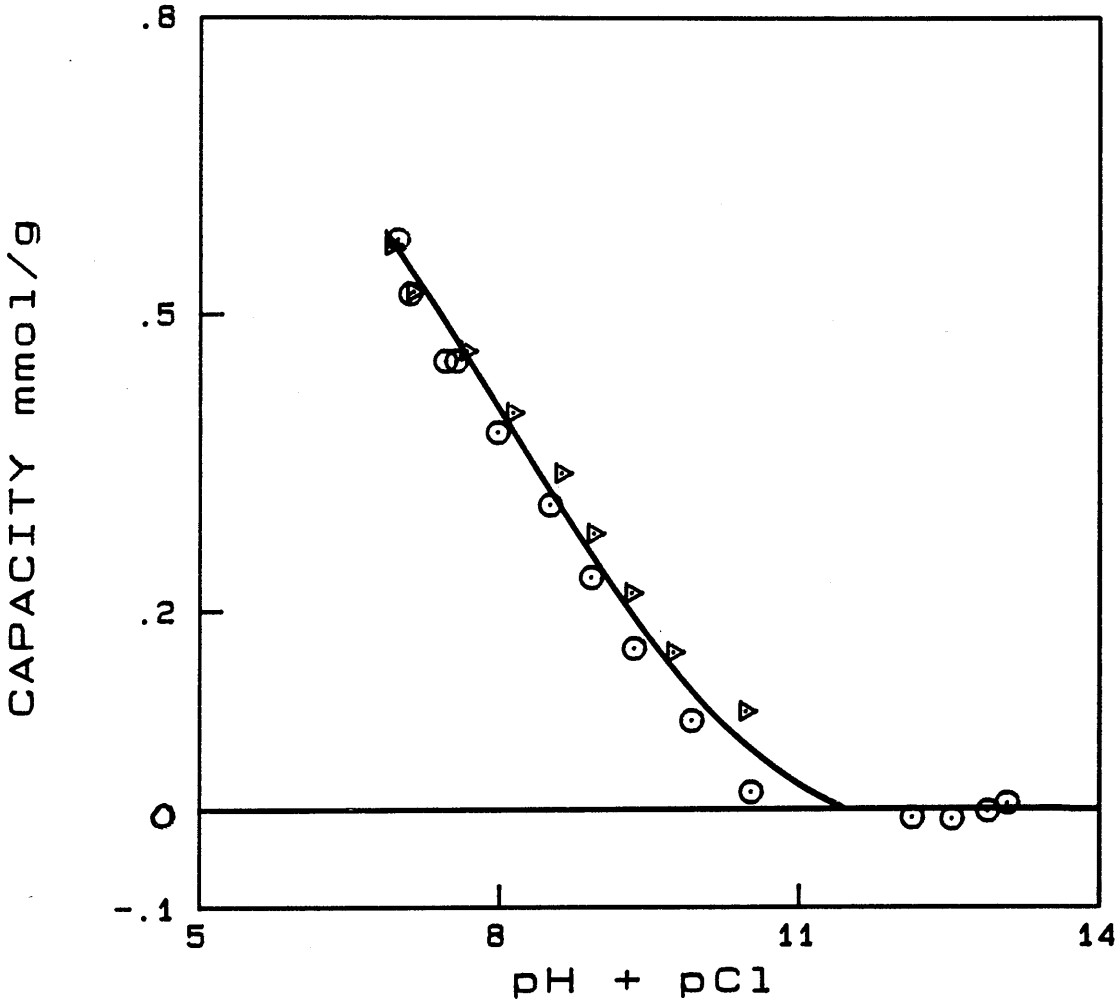


⊙ Chloride TABLE 6.2
▵ Chloride TABLE 6.1

FIGURE 6.3

CHLORIDE CAPACITY VS pHCl

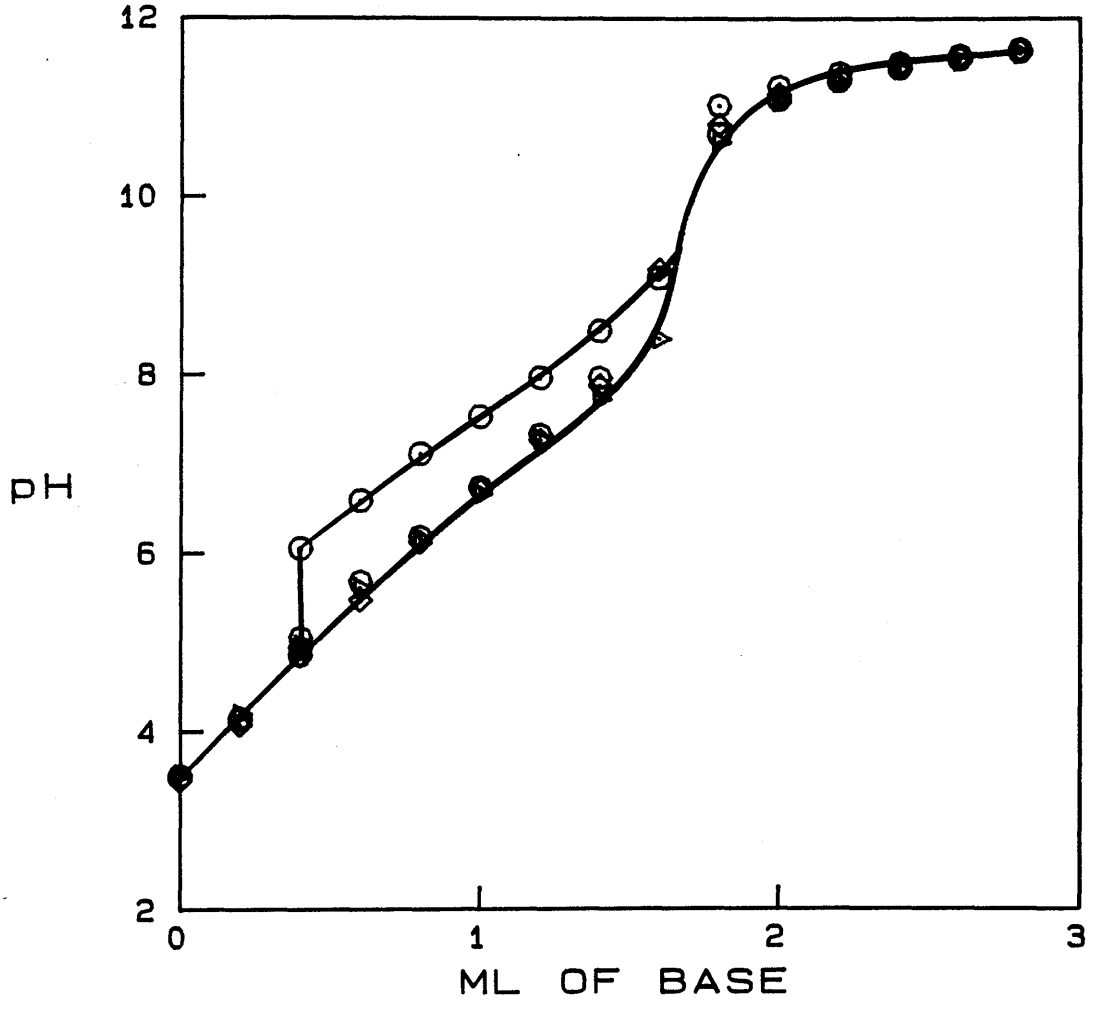
WITH AND WITHOUT ADDED NaCl



⊙ Chloride TABLE 6.2
▷ Chloride TABLE 6.1

FIGURE 6.4

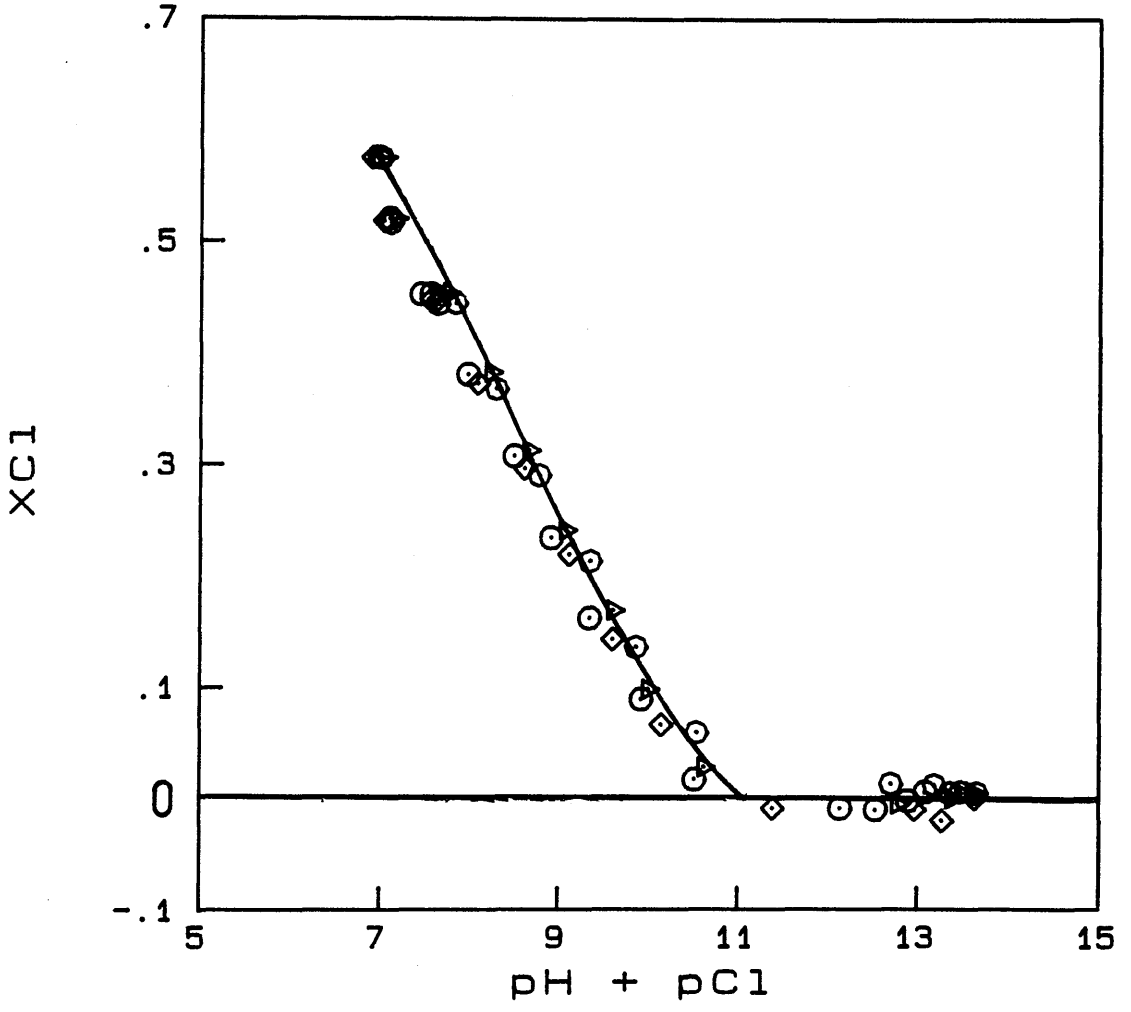
FeOOH pH TITRATIONS



⊙	CHLORIDE	TABLE 6.2
◇	PERCHLORATE	TABLE 6.3
▷	IODIDE	TABLE 6.4
⊙	BROMIDE	TABLE 6.5

FIGURE 6.5

CHLORIDE CAPACITY



⊙	CHLORIDE	TABLE 6.2
◇	PERCHLORATE	TABLE 6.3
▷	IODIDE	TABLE 6.4
⊙	BROMIDE	TABLE 6.5

FIGURE 6.6

Silver Nitrate Titration Curve of Iodide and Chloride in the Same Solution

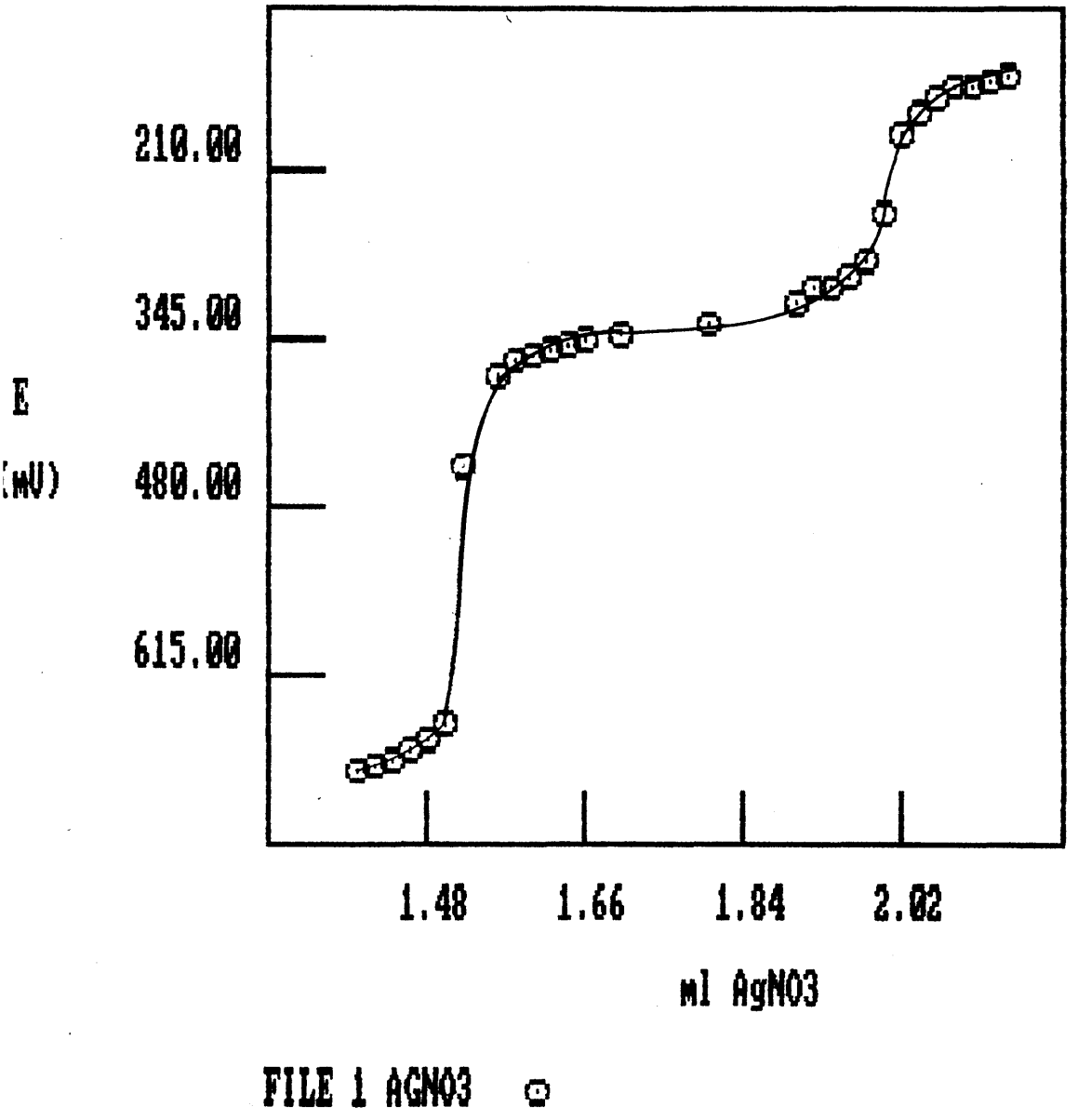


FIGURE 6.7

Gran Plot Treatment of Data from Fig. 6.6

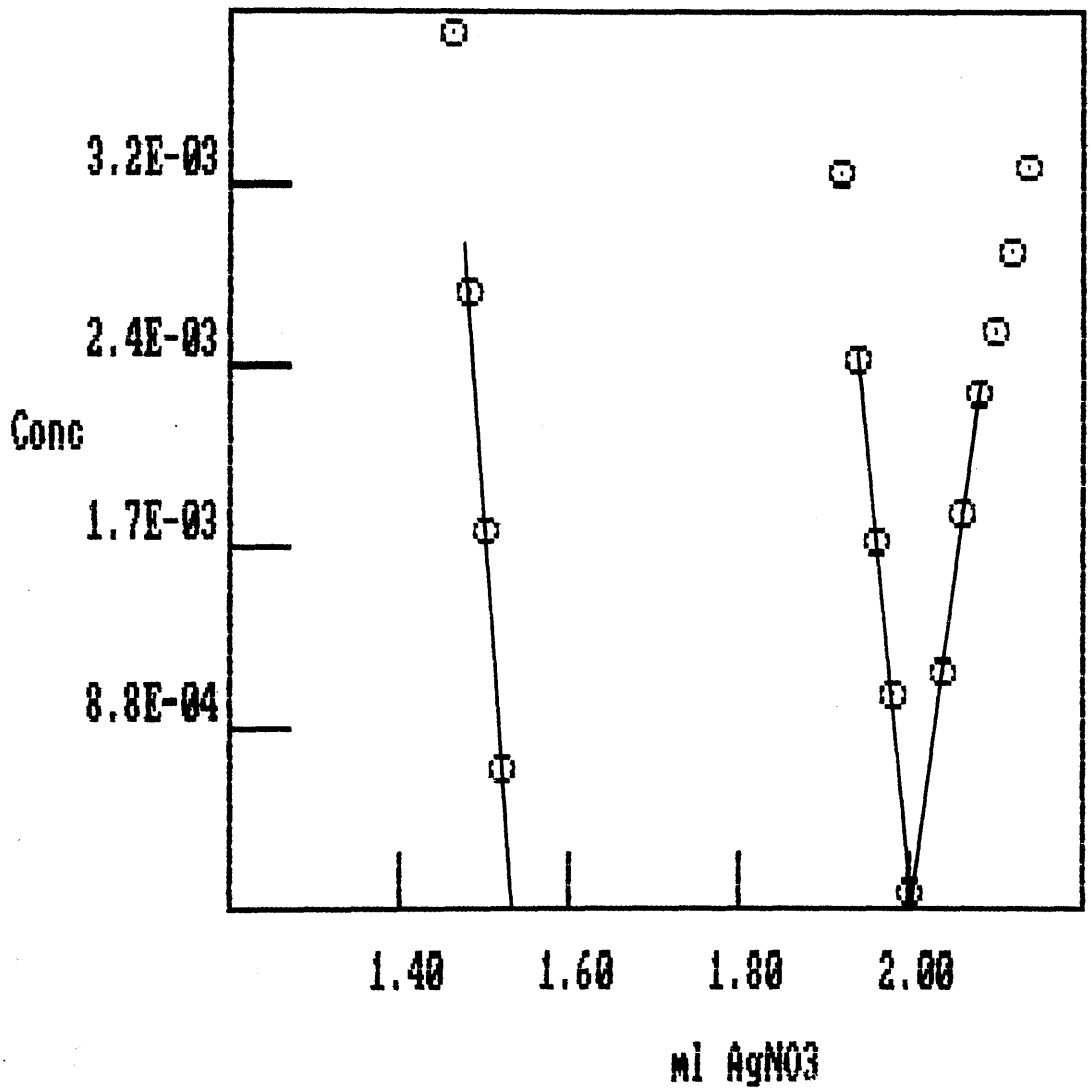


FIGURE 6.8

Chloride Capacity vs. pH with Sodium Fluoride Present

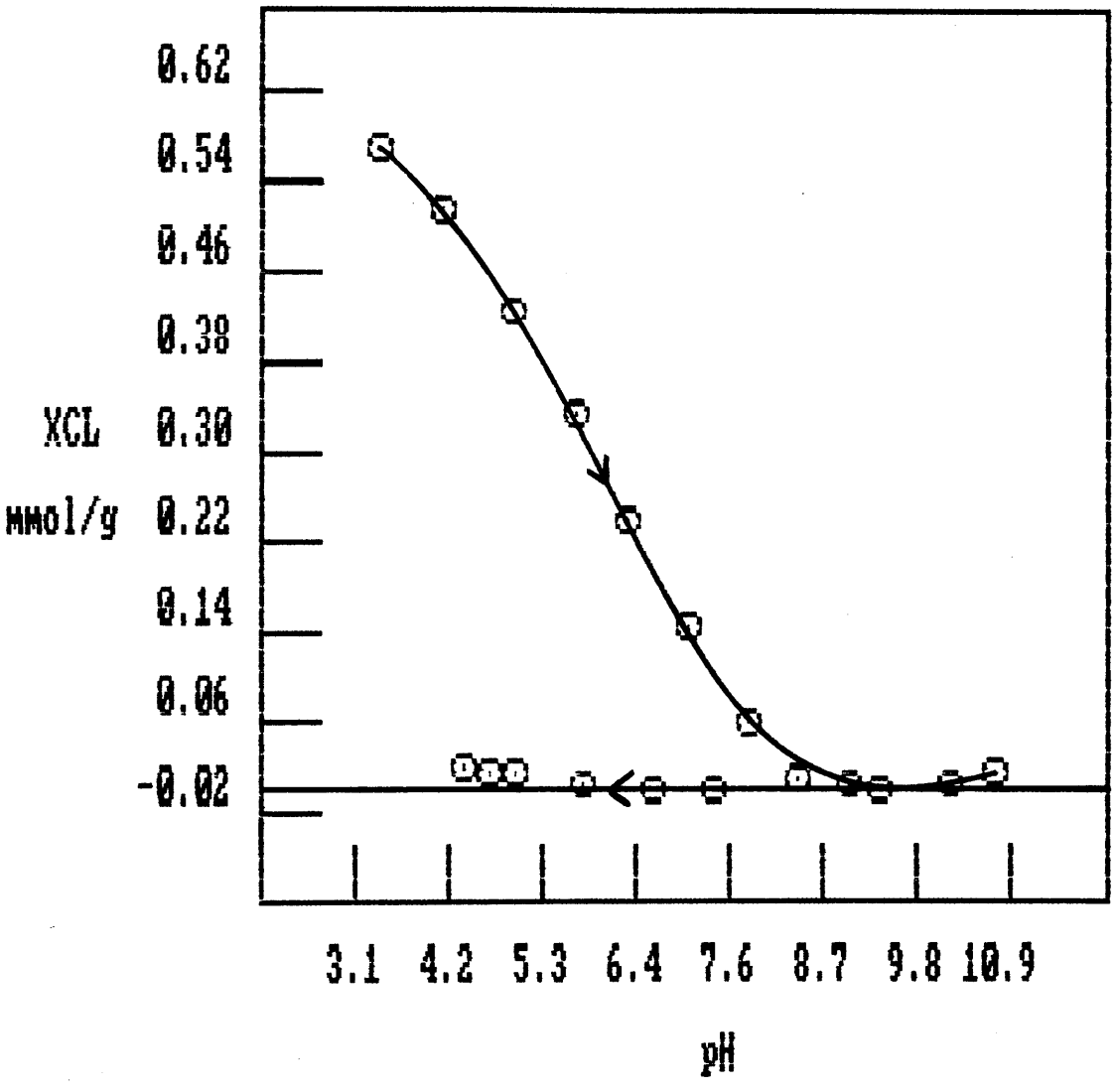


FIGURE 6.9

Distribution Coefficients of Fluoride

at pH 5 and pH 7 against pH + pF

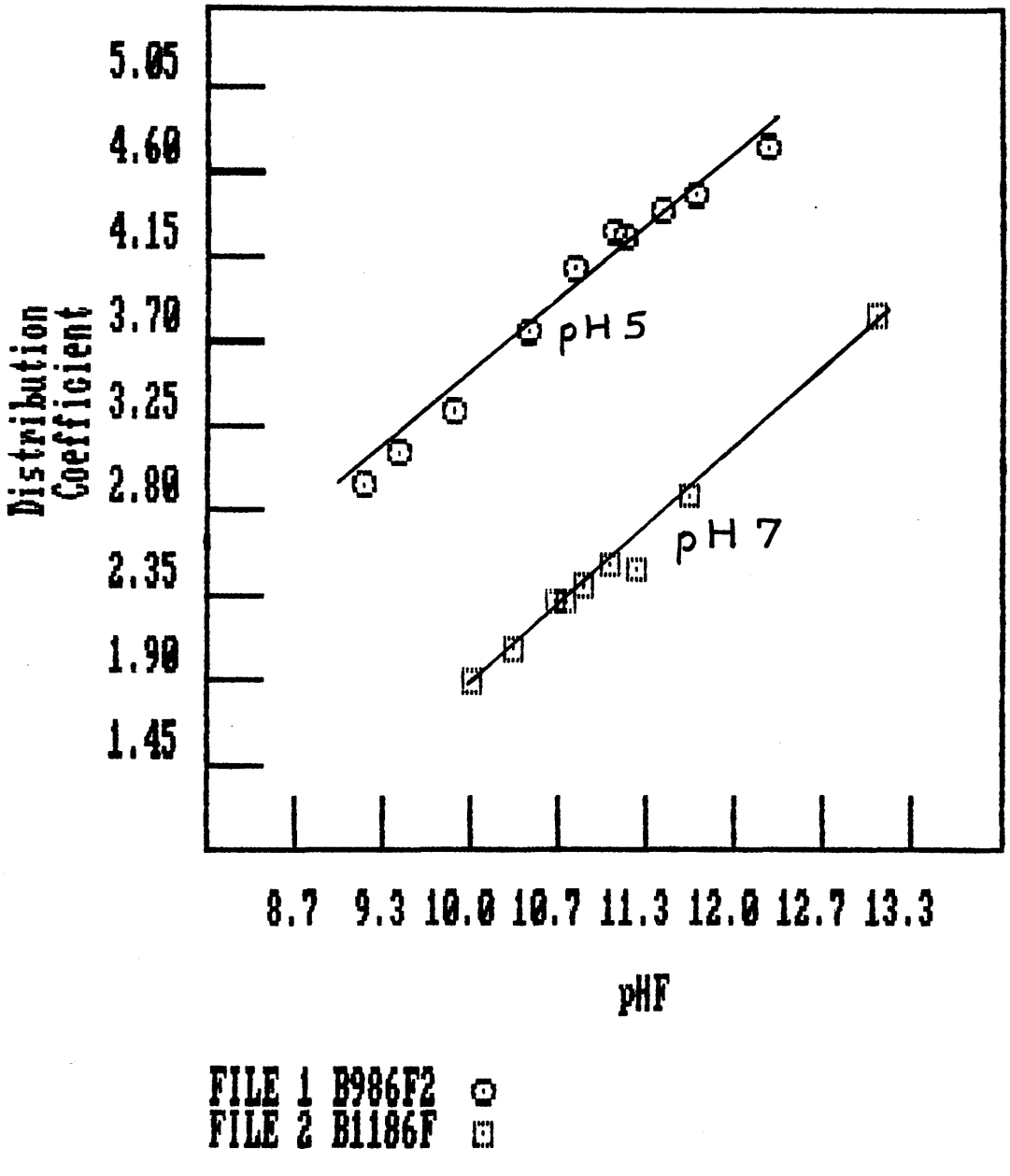
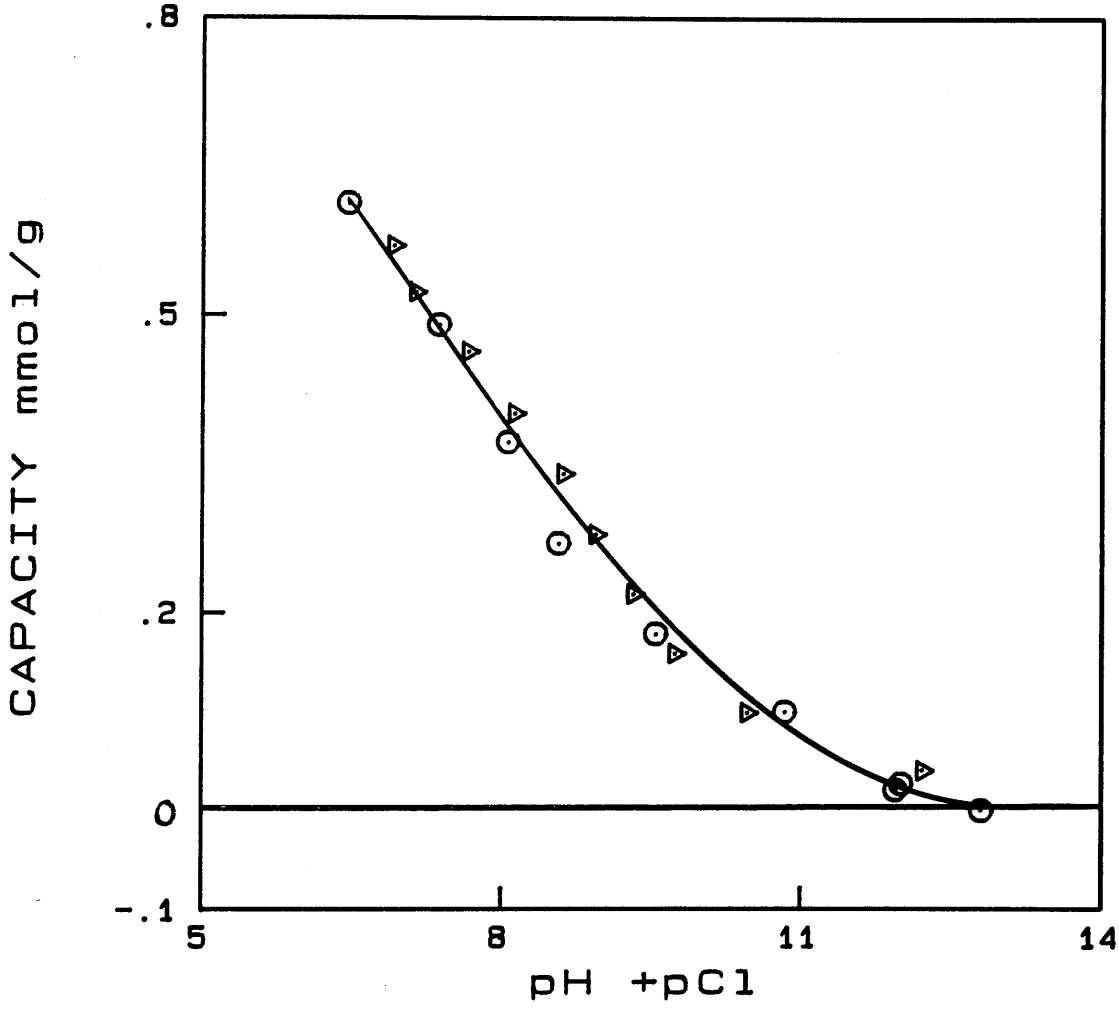


FIGURE 6.10

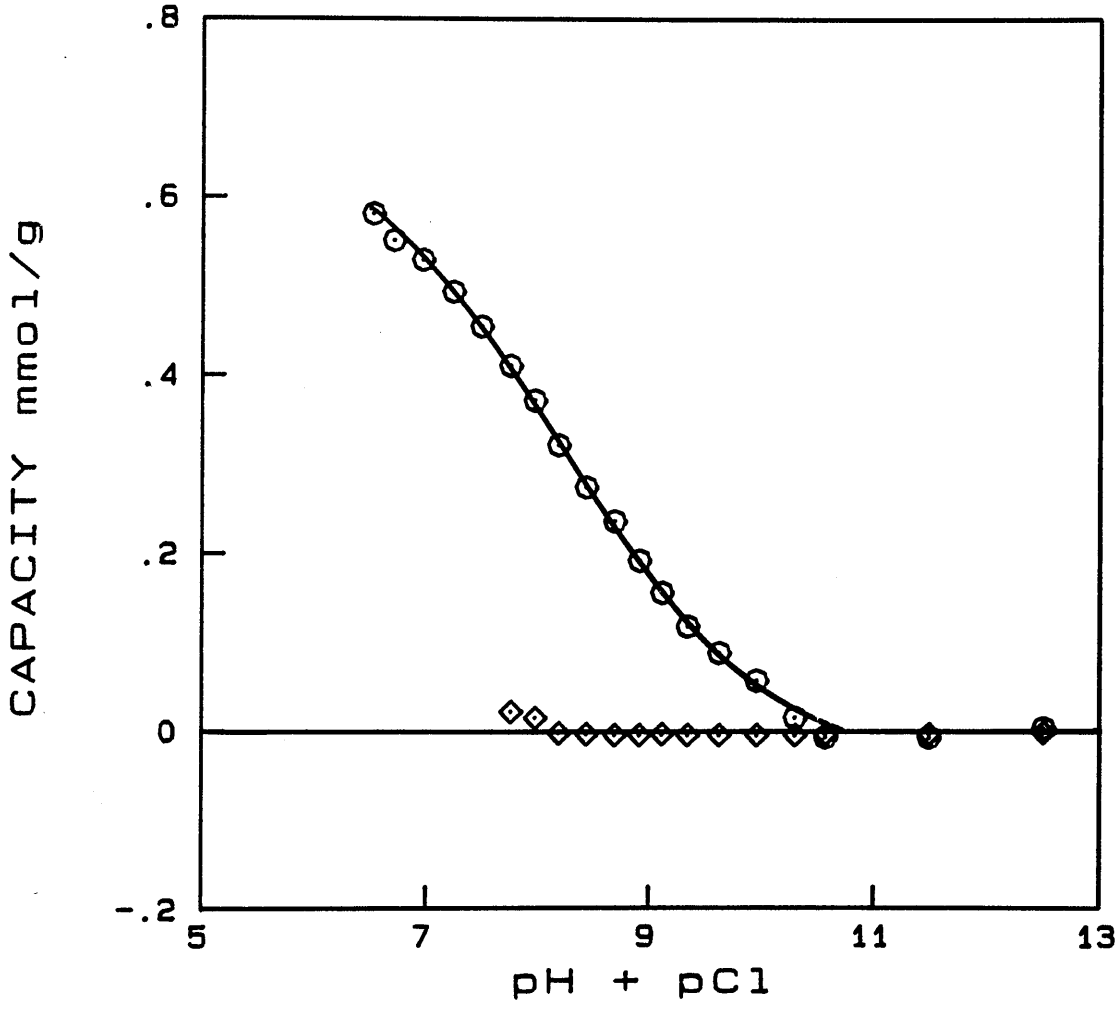
βFeOOH UPTAKE OF F & Cl



⊙ F + CL TABLE 6.8
▷ Cl ONLY TABLE 6.1

FIGURE 6.11

βFeOOH UPTAKE OF Cl & Na



⊙ Chloride TABLE 6.9
◇ Sodium TABLE 6.9

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CHAPTER 7

ION EXCHANGE PROPERTIES OF ZIRCONIA

Introduction

In the mid 1950's a large number of inorganic insoluble oxides were studied (see Chapter 1) for ion exchange at high temperatures and high radiation doses. Of the oxides for potential practical interest, zirconia was one of the most important (1). A precipitate of hydrous zirconia is formed when excess base is added to a solution of zirconyl salt. The importance of gelatinous hydrous zirconia as an ion exchanger was first recognised by Kraus and Phillips (2) who showed its anion exchange properties. Subsequent publications by Amphlett, McDonald and Redman (3) and also Merz (4) showed its amphoteric behaviour, exchanging anions in acid solutions and cations in alkali. Observations by Thomas and Owens, as early as 1935, (5) indicated that there might be salt effects upon capacity. In general, these ion exchange papers on gels recorded only pH dependence and salt effects were not discussed. In the related fields of soil science, the amphoteric behaviour of 'surface charges' on these oxides was recorded: so too was the salt (ionic strength) effect upon these surface charges. A definitive study of ion exchange and sorption on porous oxide hydroxides could not be made without a supply of good crystalline materials (in this case microcrystals of monoclinic zirconia).

For gelatinous hydrous zirconia the pH at which equal cation and anion capacities had been observed (the zero point charge) was about 7 (1-4) Kraus et al. (1) demonstrated the reversibility of bromide-nitrate exchange on hydrous zirconia and proved the process to be one of ion

exchange and not sorption. They also reported high affinities for chromate, fluoride and phosphate on hydrous zirconia. Chloride, nitrate and thiocyanate capacities of about 2 meq/g and selectivity coefficients of about 1 were also previously reported by Nancollas and Paterson for the hydrous gel material (6).

Hydrous zirconia has found various recent applications. Abe, et al. demonstrated the use of the ion exchange properties of zirconia to the separation of transition metals from large amounts of calcium in order to ease the analysis of calcium by flame technique (7). Also, Singh and Tandon have designed hydrous zirconia impregnated chromatographic paper with many rapid separation properties (8). Zirconia, therefore, is a useful ion exchange material and for such applications alone, worthy of study.

All studies so far discussed were conducted on the amorphous hydrous gel material. Clearfield (9) produced both monoclinic and cubic forms by refluxing aqueous slurries of amorphous zirconia. Monoclinic zirconia occurs naturally as the mineral baddeleyite. The easy availability of monoclinic zirconia suggested this continuing study of capacity, and its dependency on pH and salt effects, on well-defined crystal matrices.

A possible structure for zirconia was postulated by Blumenthal (10) and by Clearfield (11). Clearfield's structure was based upon the tetrameric complex cation, $[Zr(OH)_2.4H_2O]_4^{8+}$, found in the crystal structure of zirconyl chloride. Base addition was considered to give a random 'polymerization', in which hydroxyl bridges link

tetramers to give $[Zr(OH)_{2+n}.(4-n)H_2O]_4^{(8-4n)}$, an unstructured amorphous gel (6). His refluxing procedure ultimately transformed the amorphous gel particles into a monoclinic crystalline product. Fryer, Hutchison and Paterson (12) studied samples drawn from solution at various times during the hydrolysis and crystallisation process by electron microscopy. Their observations supported Clearfield's hypothesis.

Monoclinic zirconia ion exchanger is a rigid, insoluble three dimensional structure and therefore has no swelling of its lattice upon uptake. Capacity results for caesium, nitrate, chloride and bromide suggest that in hydrous zirconia these ions are retained in a substantially dehydrated state (13). A similar conclusion has been found by Helfferich for ion exchange processes on the zeolites (14) in which the dehydration is attributed to crystal lattice forces. Monoclinic zirconia is a distorted fluorite lattice (15) which could explain the large fluoride capacity reported later in this chapter.

As seen in the electron micrograph (Plate 9) the zirconia crystals are well-defined microcrystals which make them ideal for titration analysis. Subsequent work by Paterson and Rahman (16) on monoclinic zirconia showed chloride and nitrate capacities in acidic solutions to be dependent on pH and anion concentration. Similarly sodium exchange in alkali is dependent on pH and cation concentration in the external solution. In this work a more advanced titration system was developed in which a selection of ISEs were used to give information on the multiple ionic equilibria which occurs during these

titrations of monoclinic zirconia.

7.1 Experimental

Monoclinic zirconia was prepared by the hydrolysis of zirconyl chloride using the method of Clearfield (9). Details of the preparation are given in Section 3.2.

To determine zirconia ion exchange capacity the pH and ISE titration method was used (see Section 5.1.2). In this case chloride, fluoride and sodium uptake was determined. Chloride solutions were analysed by the standardised potentiometric method, Appendix C4.3, while fluoride was analysed by the ion exchange technique given in Appendix C4.4.

Capacities calculated were referred to the weight of ZrO_2. Samples of air-dried material were ignited to constant weight at 1000 °C to obtain ZrO_2 content. Electron micrograph and electron diffraction patterns have been discussed in Section 3.3.2.

7.2 Modifications to Titration Calculations for Amphoteric Exchange

Titration uptake calculations in Chapter 5 (Section 5.2.1) related to βFeOOH, which is analysed as an anion exchanger in acid solutions, but has no cation exchange properties even in alkali due to its exclusion of sodium, the potential counterion. Zirconia is amphoteric, exchanging anions in acid solutions and cations in alkali. Its crystals have an open structure, as shown in high resolution transmission electon micrographs (Plate 9) and consequently, no ion sieving characteristics were expected. Therefore, the analytical and titration procedures effectively described with the iron system were modified to include cation exchange found in zirconia.

The capacity of an anion exchanger has a pA dependency, where pA = pH + pX. That is, the anion, X, has an effect on an exchangers total capacity that is of equal importance to the pH effect. By analogy, the cation (e.g. sodium) capacity on zirconia is a single-valued function of pB = pNa + pOH as has been shown previously (16) and confirmed directly in this work (Section 7.3.3). The zirconia exchanger, therefore, would obey both mechanisms depending on which type of ion is exchanging in the varying pH conditions.

The analysis of zirconia titrations by Paterson and Rahman (16) were used as the basis for the current calculations. The electrode readings were taken as the activities of the ions according to their calibrations (Section 4.5). The computer program, Uptake2, given in

Appendix P4.4, based on input information calculates the anion and/or cation exchange capacity together with the corresponding pA or pB function. With the introduction of ISEs, the fundamental change in the computer program entailed a direct point by point assessment of the uptake or release of ions in solutions to calculate ionic strengths and thereby estimate activity coefficients. The basic modification to the program, therefore, was to include the detected levels of chloride, sodium and fluoride from the electrodes rather than deduce them from the electroneutrality of the phases and the coion exclusion principle. Some of the early titrations in this thesis repeated titrations from previous studies on zirconia (16) and showed the advantages of the new system.

7.3 Results and Discussion

The ability to produce reproducible crystalline monoclinic zirconia by the method of Clearfield (9) enabled the study of ion exchange properties along with thermodynamic and mechanistic behaviour. The particles are ´star´ or ´pod´ shaped and gave single crystal diffraction pattern for monoclinic zirconia (Table 3.2). Zirconia is stable toward both acid and alkali and thus together with the smallness of the crystals make it ideal for the titration technique. The standard titration procedure (Section 5.1.2) was used. Since the sample was previously washed clear of anions, a suspension in water was almost at neutral pH. Acid was then added to reduce the pH to about 3 and then the suspension was titrated forward with base. In the alkaline region sodium chloride or sodium fluoride was added and the system backtitrated with acid. In this way, the uptake of chloride, fluoride and sodium could be monitored by varying the types of solutions used.

7.3.1 Chloride Capacity

In this case the acid used was hydrochloric and the added salt was sodium chloride. The initial addition of acid to the aqueous suspension of zirconia produced a pH which was much higher than would be expected if there were no acid uptake by the oxide hydroxide. In consequence, the initial capacity for chloride was large and negative after the addition of acid, Table 7.1. The addition of sodium hydroxide caused the chloride capacity to decrease ultimately becoming zero once more when all the acid originally added had been neutralised. Subsequent addition of base corresponds to sodium hydroxide uptake by the exchanger which above pH 7 is a cation sorbent.

The results of pH and chloride electrode titrations with and without added sodium chloride are given in Table 7.1 and 7.2. Added salt raises the pH in acidic solution and reduces it in the alkaline region. Large capacity for chloride was shown at low pH. This is shown by the previously established mechanism, Eq. [7.1], where an increase in chloride concentration in solution would shift the equilibrium to the right in favour of uptake. In Fig. 7.1 the pH versus capacity curves, from both sets of data in Table 7.1 and 7.2, intersect at capacity = 0 at pH 7.

$$\overline{\text{ZrOOH}} + \text{H}^+_{\text{aq}} + \text{Cl}^-_{\text{aq}} = \overline{\text{ZrOOH}_2^+} + \overline{\text{Cl}^-} \qquad \text{Eq. [7.1]}$$

The data of Table 7.1 and 7.2 show clearly that neither anion nor cation capacities are single-valued functions of pH. They depend on the concentration of

sodium chloride and pH.

Like βFeOOH (Chapter 6) it was considered that anion exchange was due to a 'protonation' of a hydroxyl site, accompanied by migration of chloride counterions to provide overall electroneutrality (Eq. [7.1]). By analogy with the arguments for anion exchange on βFeOOH (Section 6.2) the anionic capacity would be expected to be a single-valued function of the activity of the whole acid (HCl) in solution. This is conveniently expressed in logarithmic form as a function of pHCl in Tables 7.1 and 7.2.

Capacity against pHCl curves are given in Fig. 7.2. Unlike the capacity versus pH curves, this plot shows that below the isoionic pH (7), where zirconia is a chloride exchanger (negative capacities) the capacity is a single-valued function of pH + pCl. In alkali when a cation mechanism (Section 7.3.3) applies the curves remain divergent. Fig. 7.3 shows the chloride capacity calculated directly from the Orion chloride electrode in comparison with the 'normal' capacity determined from the pH electrode against pHCl. The overlap of these two curves in the acid region is further verification of past techniques and the ion exchange mechanism in Eq. [7.1]. According to this proposed mechanism of anion uptake this result gives excellent confirmation that the thermodynamic prediction based on a protonation mechanism of a hydroxyl site is observed. Also, the absence of anion exchange in the alkaline region as shown by the chloride electrode in Fig. 7.3 demonstrates the null capacity for chloride anion above the exchanger's zpc.

7.3.2 Fluoride Capacity

The use of the fluoride ion selective electrode gave striking results. In an initial study, 0.4 mmol of sodium fluoride was added to a dispersion of zirconia in water. On addition of fluoride, the pH increased becoming alkaline. The original pH 5 was restored by titration with hydrochloric acid. This process was repeated sixteen times. Fig. 7.4 shows the maximum observed fluoride capacity of 8 mmol/g at pH 5. This is almost two orders of magnitude higher in capacity compared to other anions studied. This result suggests the relationship between fluoride adsorption and hydroxyl release is not necessarily simple. Fluoride must have a specific affinity for the surface zirconium atom and adsorb out of all proportion to its activity. It is suggested, based on the results of Hingston, et al. (17) for fluoride adsorption on geothite, that the fluoride ion enters the coordination layer of the surface by effecting a ligand exchange with water. A mechanism of this type is also suggested by the chloride, nitrate and perchlorate capacities of zirconia. Since the fluoride adsorption greatly exceeds the limit of chloride, nitrate and perchlorate capacities, these anions must not have any special affinity for the zirconium atoms of the oxide surface. This topic has undergone further investigation by Parfitt and Russell (18) who used infrared spectroscopy to study the complexes formed when acids are evaporated onto geothite. They postulate ligand exchange and the formation of binuclear bridging complexes. Their results for fluoride indicate that it can replace only the

singly coordinated hydroxyl groups, but does not replace hydroxyl groups which are coordinated to two or three metal atoms. They suggest the other halides only partially replace the singly coordinated hydroxyls being adsorbed as monodentate ligands.

Anion capacities on zirconia and in other oxide hydroxides studied (19,20) are associated with proton uptake. When the proton and fluoride uptake were determined using pH and fluoride electrodes, this parity was confirmed once more in Fig. 7.5. The uptake of fluoride is accompanied by the uptake of a proton or, more likely in this case, the release of a displaced hydroxyl ion from the zirconia matrix. The two mechanisms may occur simultaneously, but it is clear that the fluoride must enter the zirconia lattice because at the highest levels observed in this research (limited by the requirements of adequate electrode sensitivity) the capacities reached 8 mmol/g ZrO_2. On a molar basis, this corresponds to about one fluoride to each zirconium atom in the crystal lattice. Even for monoclinic zirconia which has a high surface area ($\approx$ 200 m^2/g) one could not expect that each zirconium was a surface atom. Consequently, lattice uptake with replacement of oxygen and bridging hydroxyls is most likely. This interpretation is supported by the observation (15) that monoclinic zirconia is a distorted fluorite lattice and so such a substitution would be facilitated.

It would not be expected that such a process would be easily reversed. Forward (NaOH) and back (HCl) titrations

were performed in the presence of sodium fluoride. The results, shown in Fig. 7.6 display the process as essentially reversible. More detailed analysis will examine whether chloride, which is increasing in this solution during this three-legged titration, is competing with fluoride for 'normal' exchange sites. However, the essential reversibility of the process is established. Hingston, et al. (21) report similar results for fluoride on goethite and gibbsite. These results of fluoride reversibility uphold their theory that when monodentate ligands form between the surface metal atom and the anion of interest, the adsorption-desorption isotherm, or forward-backward titration capacity curves, will be reversible.

As a matter of practical interest, at pH 5 if the fluoride distribution coefficient (concentration of fluoride in the exchanger over concentration of fluoride in the external solution) is plotted versus the negative logarithm of the fluoride concentration, pF, an essentially straight line occurs. This is apparent over a concentration range 10^{-5} to 10^{-2} molar in Fig. 7.7. At pF 4 the distribution coefficient is 10^{4} to 1. The zirconia, therefore, has an exceptionally high capacity for fluoride and a remarkable distribution coefficient.

7.3.3 Sodium Capacity

The titration results for chloride capacity versus pHCl in Section 7.3.1 would suggest that the cation mechanism would be similar with a sodium capacity versus pNaOH relationship. The addition of base to a suspension of zirconia above pH 7 produces a pH which is lower than would be expected. That is, the uncharged exchanger at zpc on exposure to excess base will tend to exchange water for hydroxyl with concurrent uptake of sodium counterion.

The general behaviour of pH and sodium capacity results suggest strongly that an analogous mechanism, to HCl uptake in acid, of NaOH exchange applies as shown in Eq. [7.2].

$$\overline{ZrOOH_2} + Na^+_{aq} + OH^-_{aq} = \overline{ZrOOH} + \overline{Na^+} + H_2O \qquad \text{Eq. [7.2]}$$

for which an equilibrium constant, K_b, may be defined :

$$K_b = [\overline{ZrOOH}][\overline{Na}].a_{H2O} \,/\, [\overline{ZrOOH_2}].a_{NaOH} \qquad \text{Eq. [7.3]}$$

Since $\overline{K_b}$ is by definition a constant and the activity of water is constant in dilute solution, the activities of sodium and hydroxyl in solution will determine all the activities in the exchanger. Therefore, the capacity would be a single-valued function of the activity of the whole base, conveniently expressed as pB = pNa + pOH.

To test this theory capacity is plotted as a function of pNaOH in Fig. 7.8. The results are shown in Tables 7.1 and 7.2, with and without added sodium chloride. Addition

of salt now provides additional sodium counterions in solution. This displaces the equilibrium (Eq. [7.2]) into the exchanger, transferring more cation into it. The resulting increase in the internal electrical potential, due to the new sodium ions, causes the electrochemical potential for hydroxyl species inside the exchanger to decrease and so cause hydroxyl to enter. The overall effect is that addition of salt in alkali causes increased uptake of base, raising capacity by hydroxyl removal from the external solution, thereby lowering the pH in solution. Fig. 7.8 displays the base uptake curves, completely superimposable and remain divergent in acid where the anion exchange mechanism applies (Section 7.3.1). This shows that salt system base capacity is indeed a single-valued function of pB as required by theory.

Table 7.1 Zirconia Titration Without Added NaCl

NAME OF FILE =ZR486

Concentration of NaCl = 0.00 M Concentration of NaOH = 0.108 M

Concentration of HCl = 0.10 M Initial Volume = 25.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of Acid, ml. VS = Volume of Salt, ml.

XCl = Cl^- Capacity in mmol/g XH = H^+ Capacity in mmol/g

N	VB	VA	VS	pH	pHCl	XCl	XH
1	0.00	0.00	0.00	6.13	10.997	0.000	-0.000
2	0.00	1.00	0.00	2.80	5.588	-0.265	-0.272
3	0.20	1.00	0.00	3.05	5.811	-0.251	-0.256
4	0.40	1.00	0.00	3.47	6.177	-0.216	-0.226
5	0.50	1.00	0.00	3.78	6.444	-0.187	-0.197
6	0.60	1.00	0.00	4.22	6.829	-0.145	-0.159
7	0.70	1.00	0.00	4.80	7.346	-0.097	-0.114
8	0.74	1.00	0.00	5.02	7.552	-0.079	-0.094
9	0.80	1.00	0.00	5.51	8.004	-0.043	-0.064
10	0.84	1.00	0.00	5.94	8.414	-0.021	-0.044
11	0.88	1.00	0.00	6.73	9.183	0.001	-0.024
12	0.92	1.00	0.00	7.61	10.066	0.006	-0.003
13	0.96	1.00	0.00	8.18	10.635	0.006	0.017
14	1.00	1.00	0.00	8.49	10.943	0.005	0.037
15	1.04	1.00	0.00	8.75	11.204	0.006	0.058
16	1.08	1.00	0.00	8.94	11.400	0.005	0.078
17	1.14	1.00	0.00	9.19	11.644	0.002	0.108
18	1.30	1.00	0.00	9.65	12.108	0.003	0.186
19	1.40	1.00	0.00	9.83	12.291	-0.001	0.234
20	1.50	1.00	0.00	9.98	12.451	0.001	0.281
21	1.70	1.00	0.00	10.24	12.714	-0.002	0.372
22	1.90	1.00	0.00	10.45	12.923	-0.004	0.460

Table 7.2 Zirconia Titration with Added NaCl

NAME OF FILE =ZR486HCL

Concentration of NaCl = 1.00 M Concentration of NaOH = 0.108 M

Concentration of HCl = 0.10 M Initial Volume = 25.00 ml

N = Number of data set. VB = Volume of base, ml.

VA = Volume of Acid, ml. VS = Volume of Salt, ml.

XH = H^+ Capacity in mmol/g

N	VB	VA	VS	pH	pA	pB	XH
1	2.40	1.60	1.50	9.90	11.250	5.450	0.381
2	2.44	1.90	1.50	9.54	10.888	5.807	0.286
3	2.44	2.06	1.50	9.29	10.636	6.056	0.225
4	2.44	2.20	1.50	9.02	10.364	6.324	0.170
5	2.44	2.30	1.50	8.84	10.183	6.503	0.131
6	2.44	2.40	1.50	8.57	9.912	6.772	0.092
7	2.44	2.50	1.50	8.23	9.571	7.111	0.053
8	2.44	2.60	1.50	7.81	9.150	7.530	0.014
9	2.44	2.70	1.50	7.33	8.669	8.009	-0.026
10	2.44	2.80	1.50	6.82	8.162	8.522	-0.065
11	2.44	2.95	1.50	5.90	7.244	9.444	-0.124
12	2.44	3.00	1.50	5.69	7.035	9.655	-0.144
13	2.44	3.10	1.50	5.30	6.646	10.046	-0.183
14	2.44	3.20	1.50	4.98	6.327	10.367	-0.222
15	2.44	3.30	1.50	4.69	6.038	10.658	-0.260
16	2.44	3.40	1.50	4.46	5.809	10.890	-0.297
17	2.44	3.50	1.50	4.28	5.630	11.071	-0.334
18	2.44	1.60	1.50	3.88	5.232	11.473	-0.401

FIGURE LEGENDS FOR CHAPTER SEVEN

Fig. 7.1 Capacity (mmol/g) versus pH determined by the hydrogen electrode for monoclinic zirconia. Data from Table 7.1 and 7.2, without and with added NaCl, are shown to intersect at about pH 7.

Fig. 7.2 Capacity results, as in legend Fig. 7.1, versus pH + pCl for monoclinic zirconia. Thw two curves overlap in the acid range and remain divergent in alkali. The anion capacity, therefore, is shown to be dependent upon pH and chloride ion concentration.

Fig. 7.3 Chloride capacity (mmol/g) results on zirconia against pH + pCl displayed by the hydrogen and the chloride electrode. As confirmation of earlier conclusions, the chloride electrode shows the same capacity as the hydrogen electrode in acidic pH and levels off at zero in the alkaline pH range, where the hydrogen electrode displays cation (sodium) uptake.

Fig. 7.4 Fluoride capacity (mmol/g) results on zirconia versus pH displayed by the fluoride electrode. On addition of successive aliquots of 0.4 mmol NaF, pH excusions became progressively smaller. pH was restored with HCl. Zirconia has a maximum observable capacity of 8 mmol/g at pH 5.

Fig. 7.5 Uptake of fluoride is matched with a corresponding uptake of hydrogen ion or release of hydroxyl ion from the zirconia matrix.

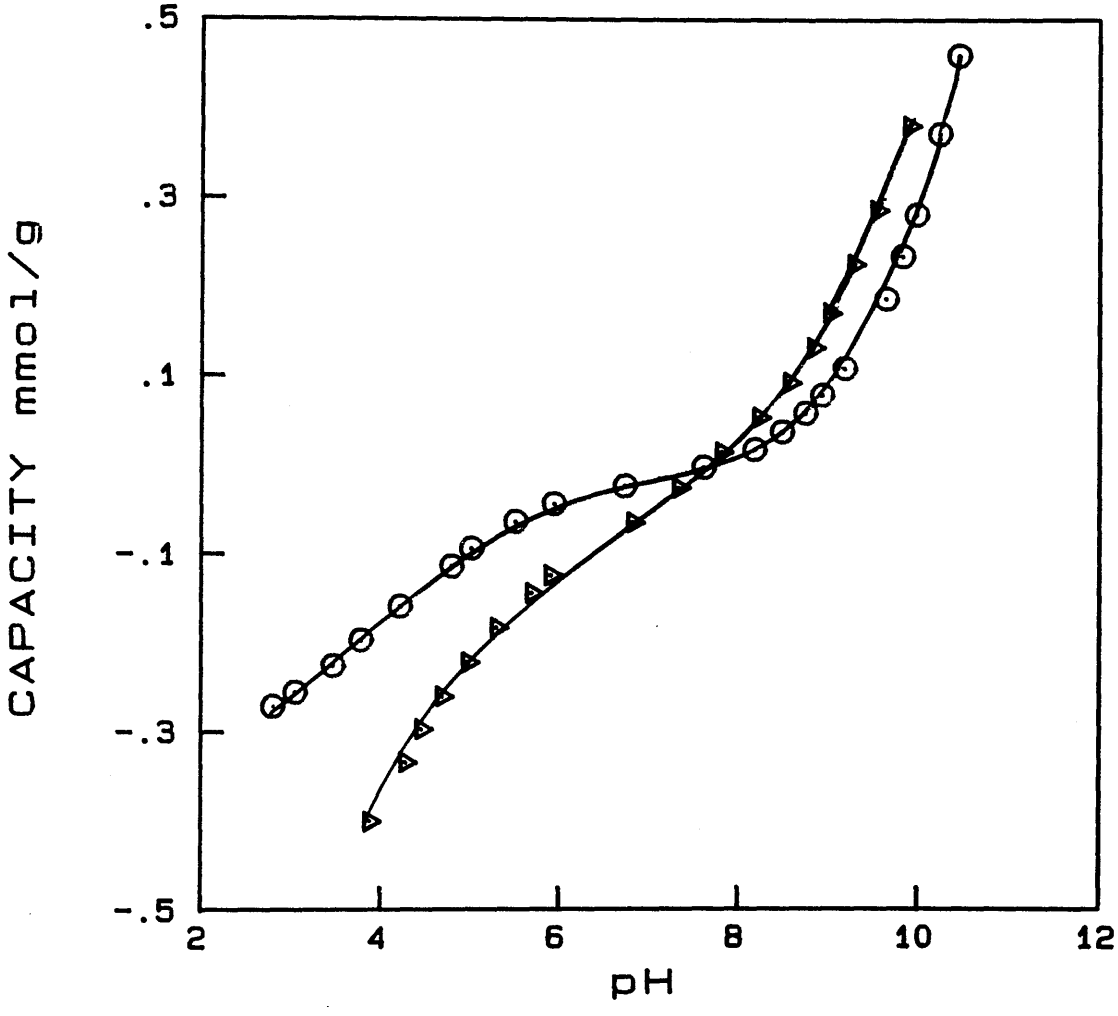
Fig. 7.6 The uptake of fluoride on the monoclinic zirconia exchanger is essentially reversible. NaF is added at pH 10 (1) and the system is backtitrated with HCl to pH 5 (2), then titrated forward with NaOH (3) and back again (4).

Fig. 7.7 Fluoride distribution coefficient, with data from Fig. 7.4, against pF. The distribution coefficient, defined as the ratio of the concentration of fluoride in the exchanger (mmol/g) to the concentration of fluoride in the external solution (mmol/ml), versus pF results in a straight line.

Fig. 7.8 Capacity results from Table 7.1 and 7.2 determined by the hydrogen electrode versus pOH + pNa. Overlap in the alkaline region shows the cation capacity to be dependent upon pOH and sodium ion concentration.

FIGURE 7.1

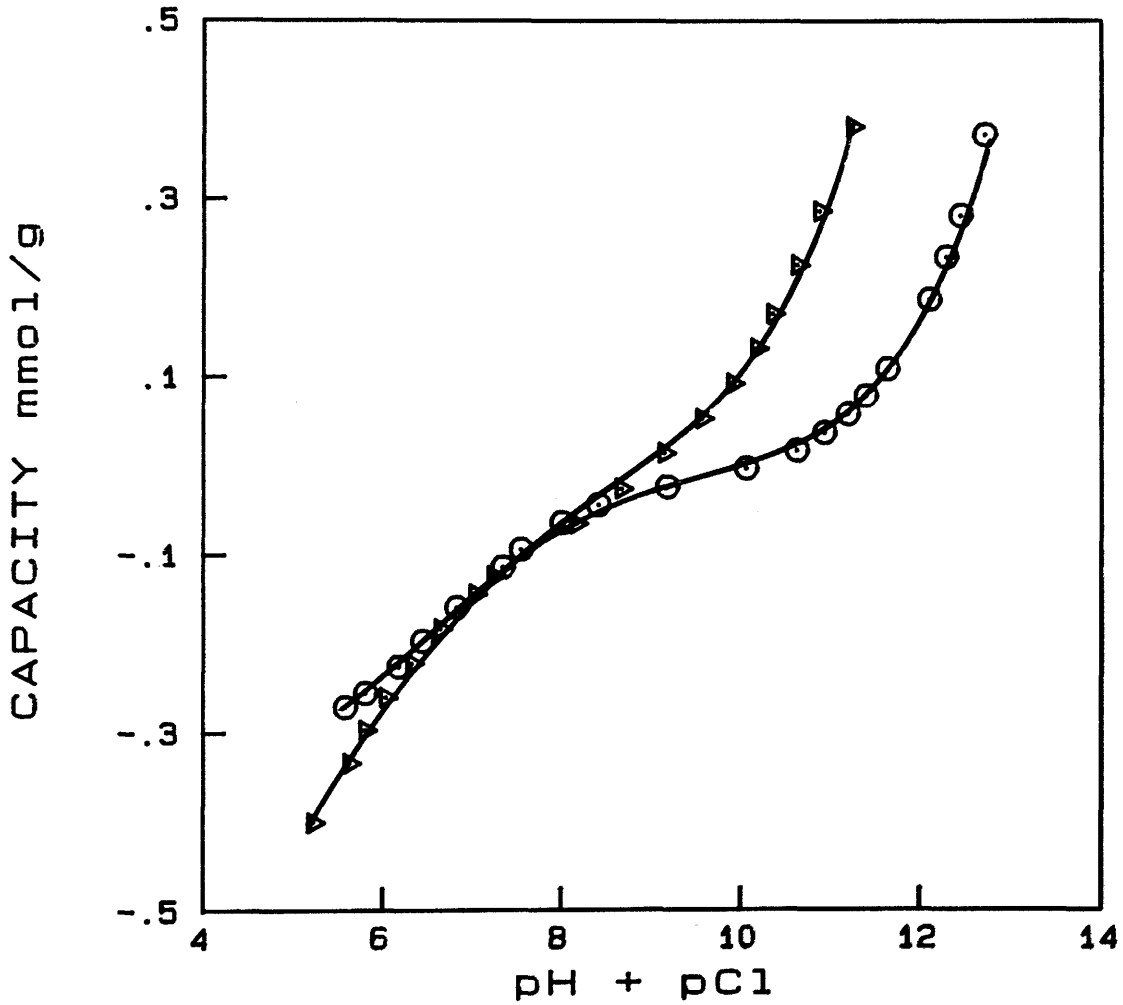
CAPACITY VERSUS pH CURVES



⊙ WITHOUT NaCl TABLE 7.1
▷ WITH NaCl TABLE 7.2

FIGURE 7.2

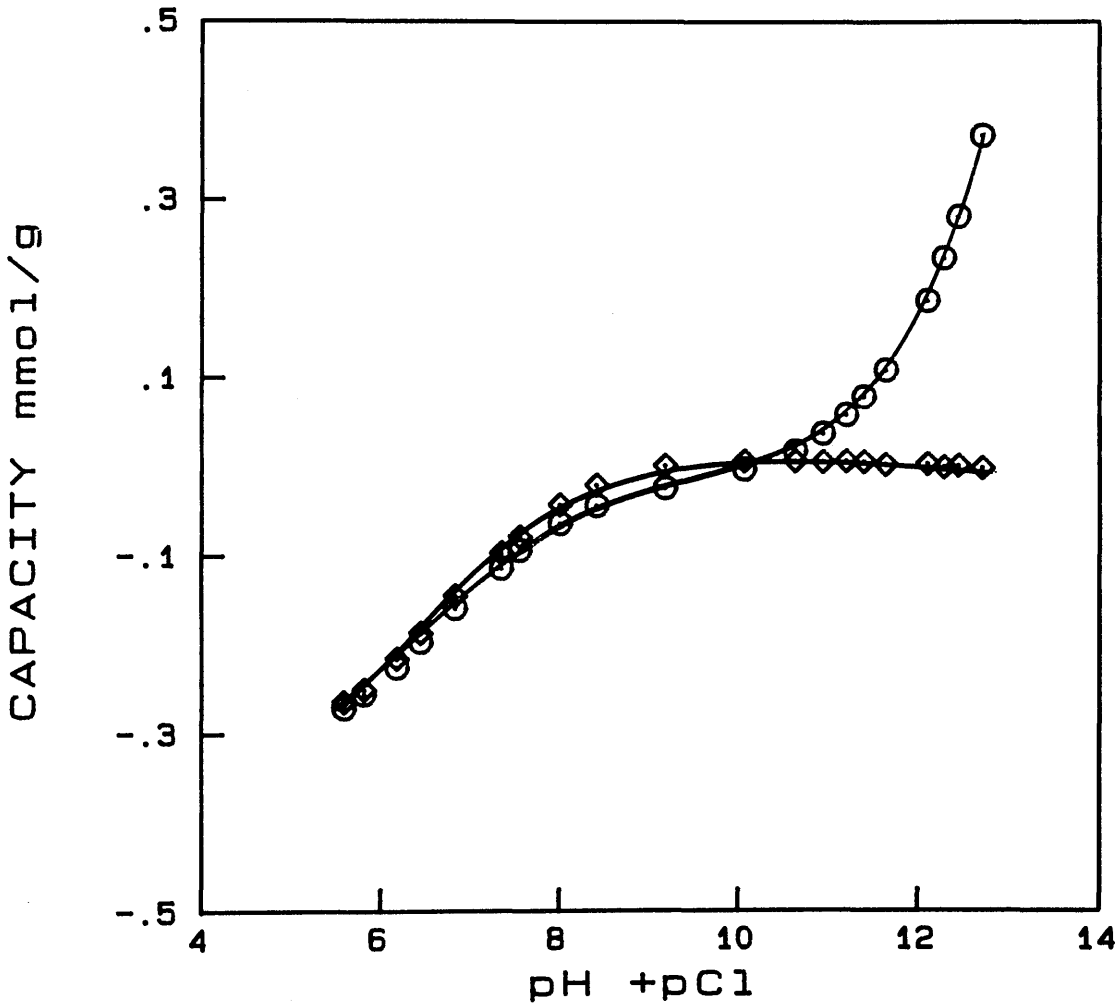
CAPACITY VS pHCl CURVES



⊙ WITHOUT NaCl TABLE 7.1
▶ WITH NaCl TABLE 7.2

FIGURE 7.3

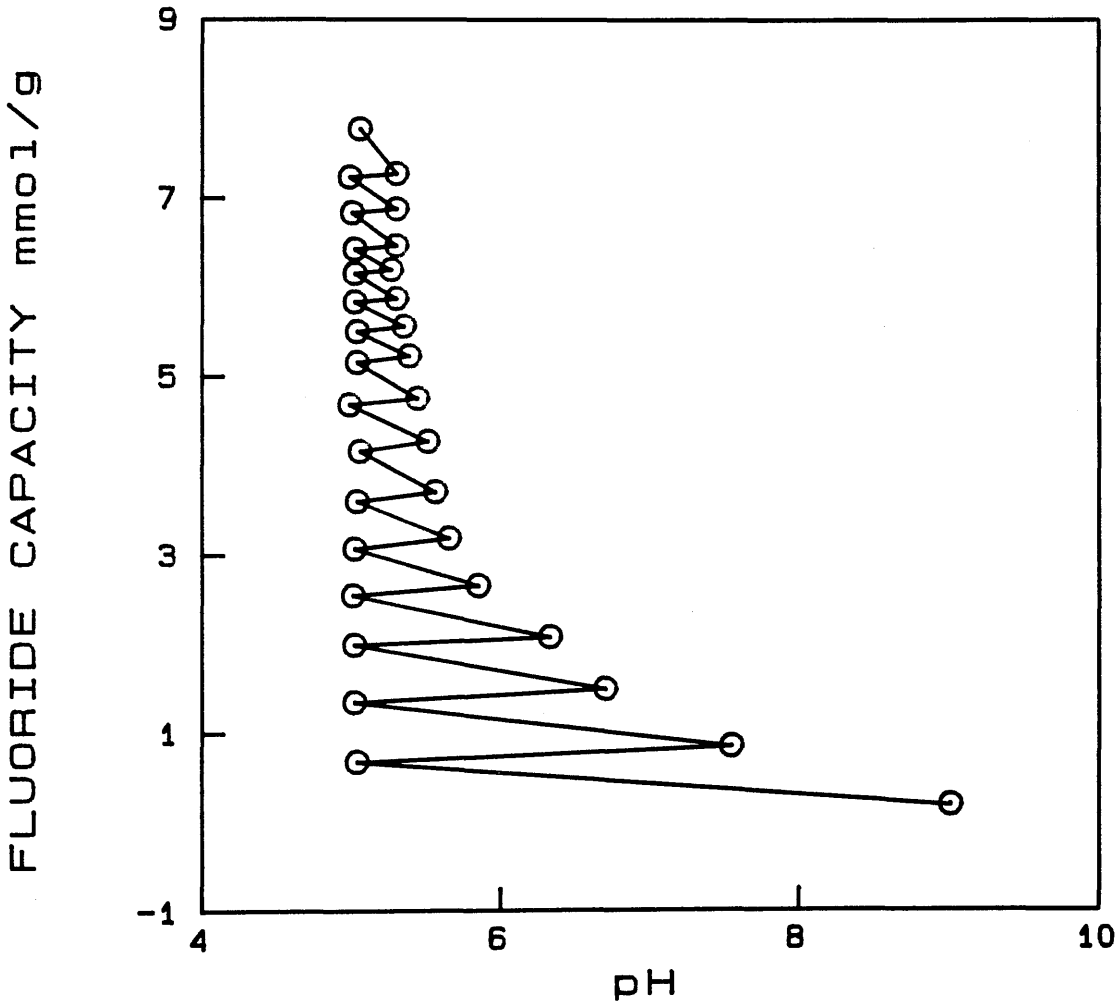
XCl BY Cl & pH ELECTRODES



⊙ pH ELECTRODE TABLE 7.1
◇ Cl ELECTRODE TABLE 7.1

FIGURE 7.4

F UPTAKE ON ZIRCONIA



⊙ FLUORIDE ELECTRODE

FIGURE 7.5

F UPTAKE AND OH RELEASE

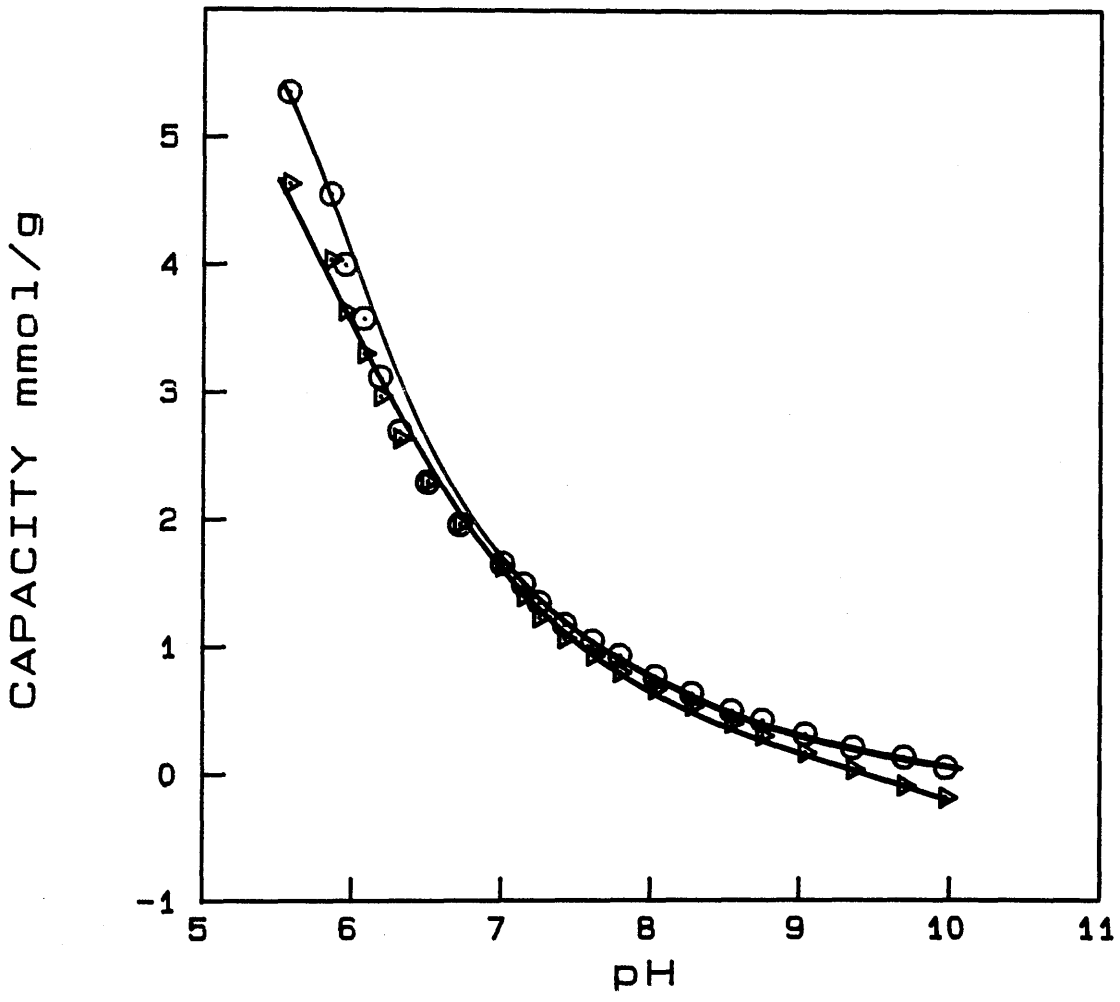
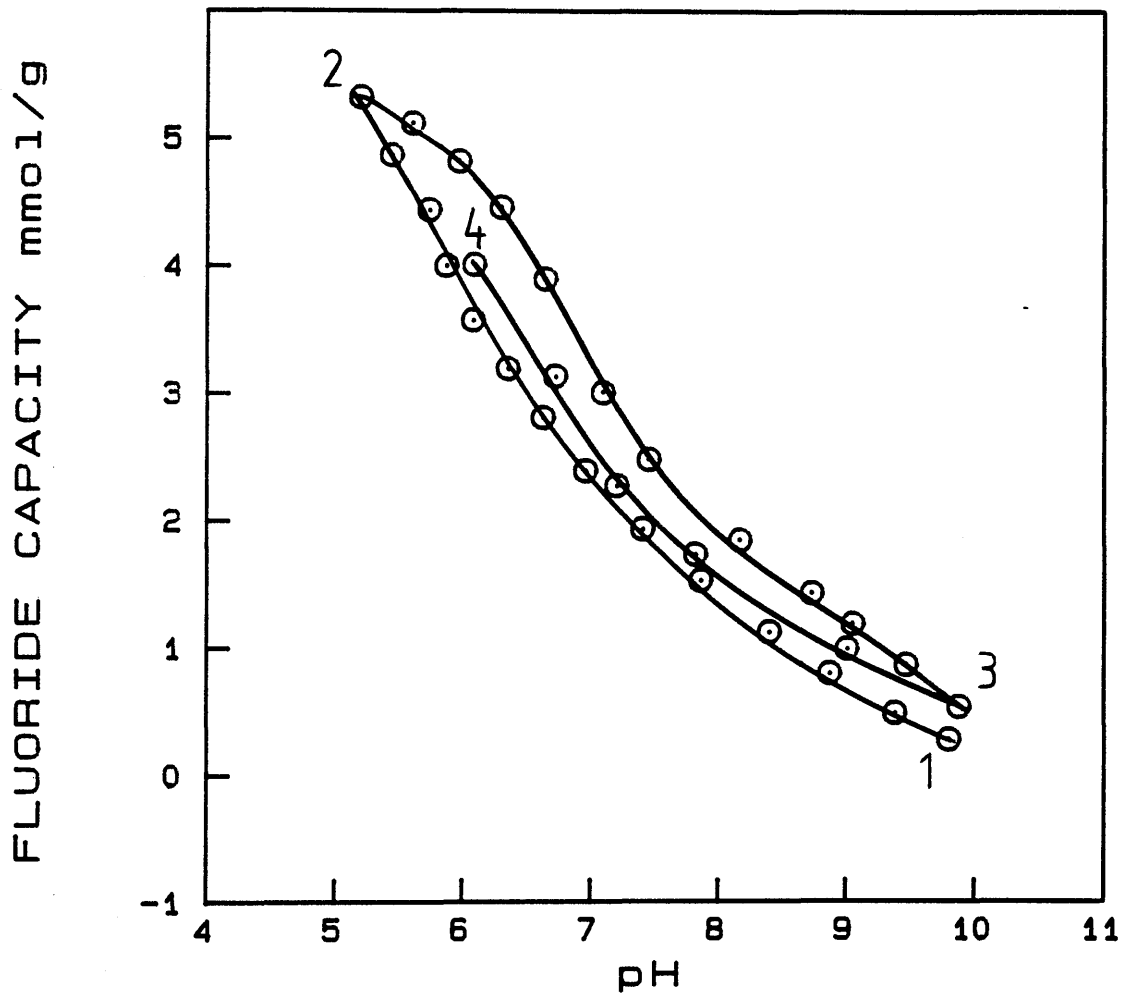


FIGURE 7.6

FLUORIDE REVERSIBILITY



⊙ FLUORIDE ELECTRODE

FIGURE 7.7

FLUORIDE DISTRIBUTION COEFFICIENT IN MONOCLINIC ZIRCONIA VERSUS NEGATIVE LOG FLUORIDE CONCENTRATION

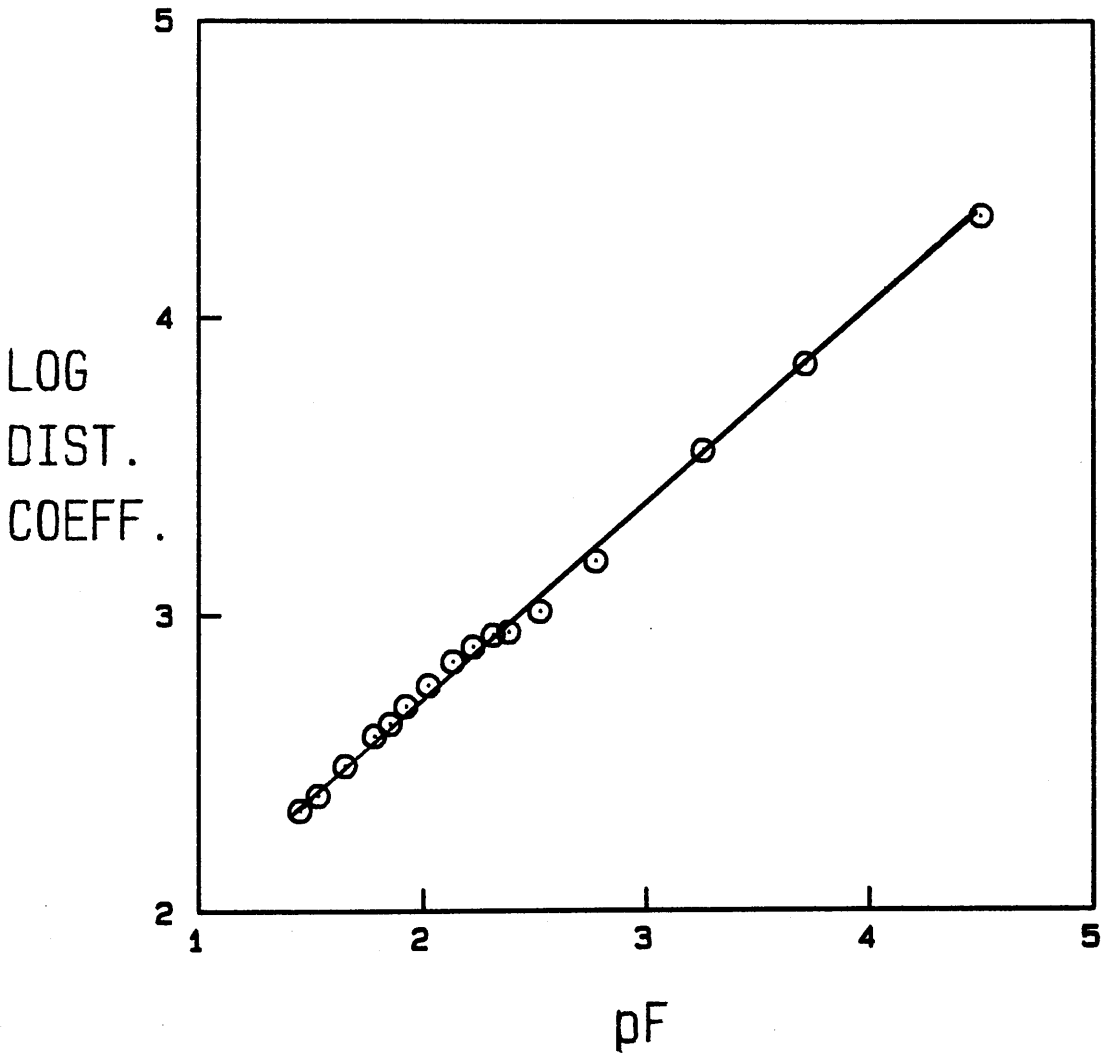
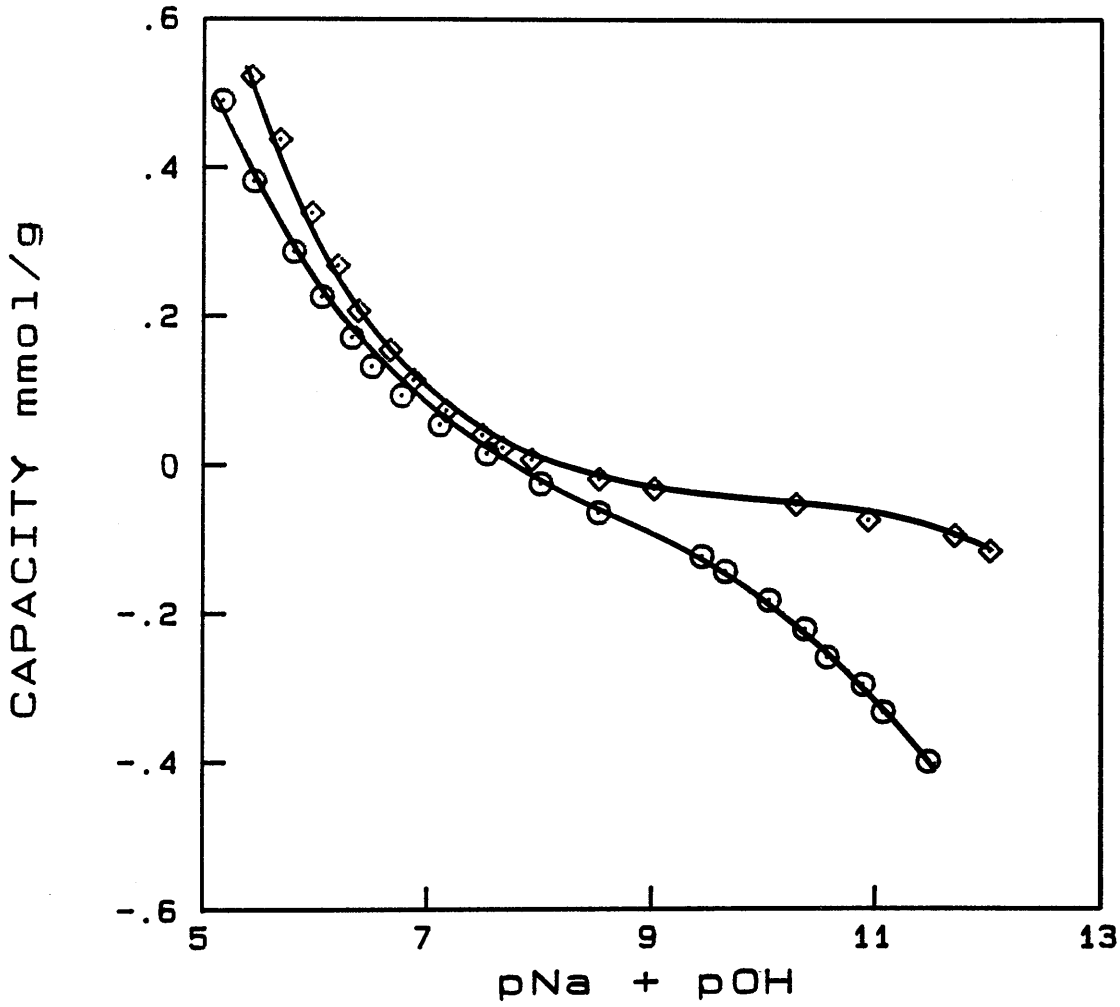


FIGURE 7.8

CAPACITY VERSUS pNa + pOH

WITH AND WITHOUT ADDED NaCl



⊙ pH ELECTRODE
◇ pH ELECTRODE

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APPENDIX C4

Preparation and Analysis of Solutions

C4.1 Carbon Dioxide-free Sodium Hydroxide

C4.2 Preparation of Salt Solutions

C4.3 Analysis of Chloride, Iodide and Bromide

C4.4 Analysis of Fluoride Solutions

All chemicals used were of Analar grade. Solutions were prepared at room temperature (25 °C) using distilled water and calibrated grade-A glassware.

C4.1 Carbon Dioxide-free Sodium Hydroxide

Fresh sodium hydroxide reagent was prepared once every two weeks. A round bottomed flask with automatic burette attachment, suitably protected from the atmosphere with soda lime columns was used. Apparatus was cleaned and new soda lime tubes prepared. About 900 ml distilled water was placed in the flask and nitrogen gas bubbled through for at least one hour. Addition of 100 ml of 1 M sodium hydroxide solution from a Volucon ampoule was made through the flask side arm under a nitrogen atmosphere. The reagent was then mixed well, all stopcocks shut and the nitrogen removed. These solutions were standardised against weighed samples of dry potassium hydrogen phthalate using phenolphthalein as indicator.

C4.2 Preparation of Salt Solutions

Salt solutions were prepared by dissolving the desired amounts of the appropriate salt in distilled water made up in grade-A volumetric flasks. Chloride, iodide and bromide solutions were analysed by potentiometric methods while fluoride solution by ion exchange techniques which are discussed below.

C4.3 Analysis of Chloride, Iodide and Bromide

The titrant, standard silver nitrate solution, was contained in a 5 ml grade-A burette which had a silver wire sealed into it below the stopcock. The tip of the burette was dipped into the solution containing the halides: iodide or bromide and chloride. The solution was stirred by a magnetic stirrer and had a silver/silver chloride (iodide or bromide) electrode dipping into it. The two electrodes were connected to a 'Solartron' 7151 computing multimeter which measured the emf of the cell directly. Additions of silver nitrate solution were made from the burette. After thorough mixing of the solution, the stirring was stopped and the system left for a few minutes until a steady reading was obtained on the voltmeter. This potential, together with the burette reading, was noted. The end point of the titration was determined by the Gran plot method (see Section 6.1.2) using the computer program given in Appendix P4.1.

C4.4 Analysis of Fluoride Solutions

Sodium fluoride was analysed by an ion exchange technique. The polystyrene quaternary amine anion exchanger, Amberlite IR 400, was prepared in the hydroxide form by elution with 1 M sodium hydroxide solution and washed free from base with distilled water. Columns of 20 cm length and 1.5 cm internal diameter were prepared. Sodium fluoride solution containing approximately 1 meq of salt was pipetted on to the column and washed slowly

through with distilled water until no hydroxide was detectable in the effluent. The total washings which then contained an equivalent amount of sodium hydroxide were treated with excess standard hydrochloric acid and titrated against standard sodium hydroxide. This simple method proved just as accurate as the accepted alarzin blue method and with less error than a lead chlorofluoride precipitate.

APPENDIX P4.1 GRAN PLOT PROGRAM

```
10 REM GRAN PLOT PROGRAM UPDATED 14/10/86
20 REM THIS PROGRAM CALCULATES SINGLE VALENCED HALIDE CONC
ENTRATIONS
30 REM VIA AgNO3 TITRATION WHERE THE INITIAL IONIC STRENGT
H IS ZERO
40 REM N = NUMBER OF POINTS
50 REM J = NUMBER OF POINTS BEFORE THE ENDPOINT
60 REM V = INITIAL VOLUME OF SAMPLE
70 REM TE = VOLUME OF TITRANT AT ENDPOINT
80 REM M = MOLARITY OF AgNO3 TITRANT
90 REM S = SOLUBILITY PRODUCT
100 REM U = ACTIVITY OF Ag ION IN BURETTE
110 '
120 '  SOLUBILITY PRODUCTS AS FOLLOWS :
130 '              AgI = 1.5  E -16
140 '             AgCl = 1.56 E -10
150 '             AgBr = 7.7  E -13
160 '
170 S = 1.5E-16 'AgI
180 K = .0256905 'RT/F
190 I0 = 0
200 DIM E(60), T(60)
210 PRINT "CURRENT PROGRAM CALCULATES IODIDE CONCENTRATION
"
220 PRINT "TO CHANGE SOLUBILITY PRODUCT FOR ANOTHER HALIDE
 ALTER LINE 170"
230 PRINT: INPUT "FILE NAME";NM$
240 OPEN"I",#1,NM$
250 INPUT#1,N: INPUT#1,J: INPUT#1,V
260 INPUT#1,TE: INPUT#1,M
270 FOR I = 1 TO N
280 INPUT#1,E(I): INPUT#1,T(I)
290 NEXT
300 CLOSE
310 PRINT N,J,V,TE,M
```

```
320 FOR I = 1 TO N
330 PRINT E(I),T(I)
340 NEXT:LPRINT
350 LPRINT"FILENAME IS ";NM$
360 LPRINT"B = HALIDE CONC. BEFORE ENDPOINT"
370 LPRINT"A = SILVER CONC. AFTER ENDPOINT"
380 LPRINT"T = ML AgNO3 TITRANT
390 LPRINT
400 FOR I = 1 TO N
410 DEF FN A(Z) = EXP(-1.1515*(SQR(Z)/(1+SQR(Z)))-.3*Z)
420 U = M * FN A(M)
430 A = EXP ((K * LOG(U) - E(I))/K) ' ACTIVITY OF Ag DUE T
O SOLUBILITY OF AgI
440 B = S/A ' ACTIVITY OF HALIDE
450 IF T(I) > TE GOTO 520
460 IS = (V * IO + TE * M)/(V + T(I)) ' IONIC STRENGTH
470 B = (B - A)/FN A(IS) ' CONCENTRATION HALIDE
480 B = B * (V + T(I)) ' MMOLES HALIDE
490 PRINT "B ="B TAB(25)"T ="T(I)
500  LPRINT "B ="B TAB(25)"T ="T(I)
510 GOTO 570
520 IS = (V * IO + T(I) * M)/(V + T(I)) ' IONIC STRENGTH
530 A = (A - B)/ FN A(IS) ' CONCENTRATION EXCESS SILVER
540 A = A * (V + T(I)) ' MMOLES SILVER
550 PRINT "A ="A TAB(25) "T ="T(I)
560 LPRINT "A ="A TAB(25) "T ="T(I)
570 NEXT
580 END
```

APPENDIX P4.2 ISE CALIBRATION EQUATION PROGRAM

```
10 ' CALIBRATION EQUATION PROGRAM
20 ' FILENAME IS CALEQ
30 ' TO GENERATE A BEST FIT STRAIGHT LINE AND
40 ' CURVE FIT EQUATION FOR CALIBRATION
50 '
60 DIM PH(50),MV(50),C(50),F(50),A(50),Y(50),YY(50),LC(50)
70 DIM M(500),PHC(50),PHS(50),X(500),ML(50),ECF(50),ESL(50
)
80 DIM PES(50),PEC(50)
90 '
100 CLS : LOCATE 10,20  :  INPUT " ENTER FILE NAME = "; NM
$
110 '
120 CLS : LOCATE 10,20  : INPUT " PH   Y/N "; PH$
130 IF (PH$ = "Y") OR (PH$ = "y") THEN GOTO 190
140 IF (PH$ = "N") OR (PH$ = "n") THEN GOTO 310
150 GOTO 120
160 '
170 '   INPUT DATA FROM FILE
180 '
190 LA$ = "H"
200 OPEN "I",#1,"\PROGRAMS\DATA\" + NM$
210 INPUT#1, N
220 FOR I = 1 TO N : INPUT#1,PH(I) : INPUT#1,MV(I)  : NEXT
230 CLOSE
240 GOTO 690
260 '
270  ' THIS SECTION CHANGES CALIBRATION DATA TO p VALUES
280 '
300 CLS
310 CLS : LOCATE 10,20 : INPUT "LABEL OF ISE";LA$
320 OPEN"I",#1,"\PROGRAMS\DATA\" + NM$
330 INPUT#1,N,VO,SC,II0
340 FOR I = 1 TO N : INPUT#1,ML(I),MV(I) : NEXT
350 CLOSE #1
370 '
380 ' CALCULATE CONCENTRATIONS
```

```
390 '
400 FOR I = 1 TO N : C(I) = (ML (I) / ( V0 + ML(I) ) )* SC
 : NEXT
410 FOR I = 1 TO N : LC(I) = -LOG( C(I))/2.30285 : NEXT
420 '
450 ' CALCULATE ACTIVITY COEFFICIENTS
460 '
470 FOR I = 1 TO N
480 C(I) = C(I) + II0
490 B = SQR(C(I))
500 F(I) = EXP( -1.1513 * ( B  / ( 1 + B  ) - .3 * C(I) )
)
510 C(I) = C(I) - II0
520 NEXT
530 '
540 '   CALCULATE ACTIVITIES
550 '
560 FOR I = 1 TO N  : A(I) = F(I) * C(I) :  NEXT
580 '
590 '   CHANGE ACTIVITY TO NEG LOG AVTIVITY
600 '
610 FOR I = 1 TO N : PH(I) = - LOG(A(I)) / 2.302585
620 NEXT
630 '
660 '
670 ' SUMS FOR SOLUTION OF DETERMINENTS
680 '
690 FOR I = 1 TO N : XA = XA + PH(I) :  NEXT
700 FOR I = 1 TO N : YMV = YMV + MV(I) :  NEXT
710 FOR I = 1 TO N : X2A = X2A + ( PH(I)^2) :  NEXT
720 FOR I = 1 TO N : X3A = X3A + ( PH(I)^3) :  NEXT
730 FOR I = 1 TO N : X4A = X4A + ( PH(I)^4) :  NEXT
740 FOR I = 1 TO N : X2Y = X2Y + ( (PH(I)^2) * MV(I) ) :
NEXT
750 FOR I = 1 TO N : XY = XY + ( PH(I) * MV(I) ) : NEXT
760 '
780 '  SOLUTION OF DETERMINENTS FOR CURVE FIT
790 '
800 D1 =   (-N)*( (-X2A)*(-X4A) - (-X3A)*(-X3A) )
810 D2 =  (-XA)*( (-XA )*(-X4A) - (-X3A)*(-X2A) )
```

```
820 D3 = (-X2A)*( (-XA )*(-X3A) - (-X2A)*(-X2A) )
830 DD =  (-1) * (( D1 )-( D2 )+( D3 ))  :
840 '
850 '
860 A1 =  (-XA)*( (-X3A)*(X2Y) - (XY)*(-X4A) )
870 A2 = (-X2A)*( (-X2A)*(X2Y) - (XY)*(-X3A) )
880 A3 =  (YMV)*( (-X2A)*(-X4A)- (-X3A)*(-X3A) )
890 AA = ( ( A1 ) - ( A2 ) + ( A3 ) )  /  ( DD )
900 '
910 '
920 B1 =   (-N)*( (-X3A)*(X2Y) - ( XY )*(-X4A) )
930 B2 = (-X2A)*( (-XA )*(X2Y) - ( XY )*(-X2A) )
940 B3 = (YMV )*( (-XA )*(-X4A) - (-X3A)*(-X2A) )
950 BB = ( (-1) * ( ( B1 ) - ( B2 ) + ( B3 ) ) ) /  ( DD )
960 '
970 '
980 C1 =  (-N)*( (-X2A)*(X2Y) - ( XY )*(-X3A) )
990 C2 = (-XA)*( (-XA )*(X2Y) - ( XY )*(-X2A) )
1000 C3 = (YMV)*( (-XA )*(-X3A)- (-X2A)*(-X2A) )
1010 CC = ( ( C1) - ( C2 ) + ( C3 ) ) / ( DD )
1020 '
1030 '
1040 ' CALCULATIONS FOR BEST FIT STRAIGHT LINE
1050 '
1060 S1 = ( XY - ( ( 1 / N )* ( XA * YMV ) ) )
1070 S2 = ( X2A - ( ( 1 / N )* ( XA^2 ) )  )
1080 SS = S1 / S2
1090 YB = YMV / N
1100 XB = XA / N
1110 YYB = YB - SS*XB
1140 '
1150 ' CALCULATE pVALUE GIVEN MILLIVOLT READING AND
1160 ' EQUATION FOR STRAIGHT LINE
1170 '
1180 FOR I = 1 TO N
1190 PHS(I) = (MV(I) -YYB) /SS
1200 NEXT
1210 '
1220 '
1230 CLS : LOCATE 8,20  : PRINT "**************************
```

```
*"
1240 LOCATE 12,20 : PRINT "**************************"
1250 '
1260 '
1270 '  SUBROUTINE FOR CALCULATING pVALUE GIVEN MILLIVOLT
1280 '  READING AND SECOND ORDER EQUATION FOR CURVE FIT
1290 '  USING SUCESSIVE APPROXIMATIONS
1300 '
1310 FOR I = 1 TO N
1320 LOCATE 10,20 : PRINT " CALCULATIONS IN PROGRESS"
1330 X(1) = PHS(I)
1340 T = 1 : TB = 0
1350 T = T + 1
1360 TB = TB + 1
1370 M(T) = AA + BB * X(TB) + CC * X(TB) ^ 2
1380 IF  ABS(M(T) - MV(I)) < .001  THEN GOTO  1560
1390 '
1400 '
1410 IF M(T) > MV(I) THEN XH = X(TB)  'DEFINE HIGH VALUE F
OR X
1420 IF M(T) < MV(I) THEN XL = X(TB)  'DEFINE LOW VALUE FO
R X
1430 '
1440 '
1450 IF TB < 2.1 GOTO 1500
1460 IF X(TB) = XH THEN  X(TB+1)=(XH + XL) /2 : GOTO 1350
1470 IF X(TB) = XL THEN  X(TB+1)= (XH + XL) /2 : GOTO 1350
1480 '
1490 '
1500 IF X(TB) = XH THEN IF BB > 0  THEN X(TB+1)= .5*X(TB)
          : GOTO 1350
1510 IF X(TB) = XH THEN IF BB < 0  THEN X(TB+1) = 2*X(TB)
          : GOTO 1350
1520 IF X(TB) = XL THEN IF BB > 0  THEN X(TB+1) = 2*X(TB)
          : GOTO 1350
1530 IF X(TB) = XL THEN IF BB < 0  THEN X(TB+1) =.5*X(TB)
          : GOTO 1350
1540 '
1550 '
1560 PHC(I) = X(TB)
```

```
1570 NEXT
1580 FOR I = 1 TO N
1590 PES(I) = ( 1 - EXP((PHS(I)-PH(I))*2.30285))
1600 PEC(I) = ( 1 - EXP((PHC(I)-PH(I))*2.30285))
1610 NEXT
1620 '
1630 CLS
1640 PRINT "FILE NAME = ";NM$ : PRINT : PRINT
1650 PRINT " Y = "YYB" + "SS"X"
1660 PRINT " Y = "AA " + " BB"* X  + "CC" * X^2"
1670 PRINT : INPUT "HIT RETURN TO CONTINUE";CT$
1680 '
1690 '
1700 '
1710 CLS : LOCATE 10,30 : INPUT "WRITE TO FILE  Y/N";WF$
1720 IF (WF$ = "Y") OR (WF$ = "y") THEN GOTO 1750
1730 IF (WF$ = "N") OR (WF$ = "n") THEN GOTO 1900
1740 GOTO 1710
1750 IF LA$ = "H" THEN GOTO 1820
1760 OPEN"O",#1,"\PROGRAMS\DATA\RESULTS\" + NM$ + "_C"
1770 WRITE#1,N
1780 FOR I = 1 TO N : WRITE #1,LC(I),MV(I) : NEXT
1790 CLOSE #1
1800 '
1810 '
1820 OPEN"O",#2,"\PROGRAMS\DATA\RESULTS\" + NM$ + "_A"
1830 WRITE #2,N
1840 FOR I = 1 TO N : WRITE #2,PH(I),MV(I) : NEXT
1850 CLOSE #2
1890 '
1900 ' PRINT RESULTS ON PRINTER
1910 '
1920 CLS : LOCATE 10,30 : INPUT" PRINT RESULTS Y/N";PR$
1930 IF (PR$ = "Y") OR (PR$ = "y") THEN GOTO 1960
1940 IF (PR$ = "N") OR (PR$ = "n") THEN GOTO 2620
1950 GOTO 1700
1960 CLS
1970 LPRINT CHR$(27);"1";CHR$(12)
1980 LPRINT CHR$(27);"C";CHR$(70)
1990 LPRINT CHR$(27);"A";CHR$(18)
```

```
2000 LPRINT CHR$(27);CHR$(40)
2010 INPUT "TITLE OF TABLE";TITLE$
2020 LPRINT TITLE$ : LPRINT
2030 LPRINT "FILE NAME = ";NM$;
2040 IF (PH$ = "Y") OR (PH$ = "y") THEN GOTO 2100
2050 IF (PH$ = "N") OR (PH$ = "n") THEN GOTO 2060
2060 INPUT "CONCENTRATION OF STANDARD";CON$
2070 INPUT " INITIAL VOLUME";INV$
2080 LPRINT TAB(35)"CONC OF STANDARD = ";CON$
2090 LPRINT TAB(35)"INITIAL VOLUME = ";INV$  : LPRINT
2095 GOTO 2110
2100 LPRINT : LPRINT
2110 LPRINT "FIRST ORDER EQUATION     E = ";
2120 LPRINT USING "####.###";YYB;
2130 LPRINT " + ";
2140 LPRINT USING "###.###";SS;
2150 LPRINT " p"LA$
2160 LPRINT "SECOND ORDER EQUATION    E = ";
2170 LPRINT USING "####.###";AA;
2180 LPRINT " + ";
2190 LPRINT USING "###.###";BB;
2200 LPRINT " p"LA$" + ";
2210 LPRINT USING "###.###";CC;
2220 LPRINT "p("LA$")";
2230 LPRINT CHR$(27);"S";CHR$(0);
2240 LPRINT "2";
2250 LPRINT CHR$(27);"T";
2260 LPRINT : LPRINT : LPRINT TAB(30)"CURVE FITS"
2270 LPRINT  TAB(2)"N";TAB(8)"E";TAB(16)"* p"LA$;TAB(26)"*
* p"LA$;
2280 LPRINT TAB(38)"** p"LA$;TAB(47)"% error";TAB(57)"% er
ror";
2290 LPRINT CHR$(27);"-1";
2300 LPRINT TAB(1);TAB(7)"mV";TAB(14)"(actual)"TAB(24)"2ND
 ORDER";
2310 LPRINT TAB(35)"1ST ORDER"TAB(46)"2ND ORDER"TAB(57)"1S
T ORDER"
2320 LPRINT TAB(1);TAB(66)
2330 LPRINT CHR$(27);"-0";
2340 LPRINT
```

```
2350 FOR I = 1 TO N
2360 LPRINT I TAB(5);
2370 LPRINT USING"####.#";MV(I);
2380 LPRINT TAB(15);
2390 LPRINT USING"##.###";PH(I);
2400 LPRINT TAB(24);
2410 LPRINT USING"##.###";PHC(I);
2420 LPRINT TAB(36);
2430 LPRINT USING"##.###";PHS(I);
2440 LPRINT TAB(47);
2450 LPRINT USING"###.#";(PEC(I) * 100);
2460 LPRINT TAB(57);
2470 LPRINT USING"###.#";(PES(I) * 100)
2480 NEXT
2490 CLS : INPUT "GIVE NAME OF ION BEING MEASURED";IA$
2500 LPRINT : LPRINT "% error = % difference between the a
ctual "IA$" ion"
2510 LPRINT TAB(11)"activity and the calculated activity"
2520 LPRINT "p"LA$" = Negative log of the "IA$" ion activi
ty
2530 LPRINT
2540 IF (PH$ = "Y") OR (PH$ = "y") THEN GOTO 2560
2550 IF (PH$ = "N") OR (PH$ = "n") THEN GOTO 2580
2560 LPRINT "* Prepared pH buffer standards per Perrin( )"
2570 GOTO 2590
2580 LPRINT "* Calculated from known concentration and ion
ic strength"
2590 LPRINT "** Calculated from curve fit equation"
2600 CLS
2610 LPRINT CHR$(12)
2620 END
```

APPENDIX P4.3 CREATE2 PROGRAM

```
10 REM CREATE DATA FILE WITH ISE RAW mV UPDATED 8/8/86
20 CLS
30 H = 80
40 DIM VB(H),VS1(H),VS2(H),VA(H),E1(H),E2(H),E3(H)
50 DIM A(H),B(H),AA(H),BB(H),CC(H)
60 PRINT: INPUT"ENTER NUMBER OF ISE'S RECORDED (1,2 OR 3)
";NI
70 PRINT"FIRST ELECTRODE MUST BE pH"
80 PRINT"SECOND ELECTRODE MUST BE Cl"
90 PRINT"THREE ELECTRODES MAX."
100 PRINT: PRINT"ENTER CALIBRATION INFORMATION "
110 PRINT"IN THE FORM  Y = A + BX"
120 PRINT"IN THE FORM  Y = AA + BB(X) + CC(X^2)"
130 FOR I = 1 TO NI
140 PRINT
150 IF I = 1 THEN PRINT "PH DATA"
160 IF I = 2 THEN PRINT "CL DATA"
170 IF I = 3 THEN PRINT "ISE 3 DATA"
180 INPUT "A = ";A(I)
190 INPUT "B = ";B(I)
200 INPUT "AA = ";AA(I)
210 INPUT "BB = ";BB(I)
220 INPUT "CC = ";CC(I)
230 NEXT
240 PRINT
250 INPUT"NO. of DATA SETS ";N
260 INPUT"pH at the ISOELECTRIC POINT ";EO
270 INPUT "INITIAL VOLUME ";VO
280 INPUT "MOLARITY of BASE ";MB
290 INPUT "MOLARITY of SALT 1 ";MS1
300 INPUT "MOLARITY OF SALT 2 ";MS2
310 INPUT "MOLARITY of ACID ";MA
320 INPUT "GRAMS OF EXCHANGER ";GA
330 INPUT "GRAMS OF DRIED EXCHANGER ";GM
340 PRINT"ENTER RAW DATA. E1,E2, AND E3 CORRESPOND TO mV F
```

```
ROM PH, CL, AND ISE 3"
350 PRINT"VA IS VOLUME OF HYDROCHLORIC ACID ADDED"
360 PRINT"VS1 IS VOLUME OF CHLORIDE SALT ADDED"
370 FOR I= 1 TO N
380 PRINT: PRINT I
390 PRINT " VB, VS1, VS2, VA, E1, E2, E3"
400 INPUT "  "; VB(I),VS1(I),VS2(I),VA(I),E1(I),E2(I),E3(I
)
410 NEXT
420 PRINT: INPUT "FILENAME";NM$
430 INFILE$ = "\PROGRAMS\DATA\" + NM$
440 OPEN INFILE$ FOR OUTPUT AS #1
450 WRITE #1,N: WRITE #1,EO: WRITE #1,VO
460 WRITE #1,MB: WRITE #1,MS1: WRITE #1,MS2: WRITE #1,MA
470 WRITE #1,GA: WRITE #1,GM
480 WRITE #1,NI
490 WRITE #1,A(1): WRITE #1,B(1): WRITE #1,A(2)
500 WRITE #1,B(2): WRITE #1,A(3): WRITE #1,B(3)
510 WRITE #1,AA(1): WRITE #1,BB(1): WRITE #1,CC(1)
520 WRITE #1,AA(2): WRITE #1,BB(2): WRITE #1,CC(2)
530 WRITE #1,AA(3): WRITE #1,BB(3): WRITE #1,CC(3)
540 FOR I = 1 TO N
550 WRITE #1,VB(I),VS1(I),VS2(I),VA(I),E1(I),E2(I),E3(I)
560 NEXT
570 CLOSE #1
580 CLS
590 END
```

APPENDIX P4.4 UPTAKE2 PROGRAM

```
10 ' UPTAKE CALCULATIONS PROGRAM
20 ' FILENAME UPTAKE
30 '
40 ' A PROGRAM TO CONVERT MV READINGS FROM TITRATIONS
50 ' TO ACTIVITIES AND CONCENTRATIONS AND CALCULATE
60 ' UPTAKE OF IONS BY CRYSTALS IN THE SOLUTION
70 '
80 CLS
90 H =80
100 DIM VB(H),VA(H),E1(H),E2(H),E3(H),G(H),PHCL(H),PHF(H),
H(H)
110 DIM PH(H),PCL(H),PF(H),XX(H),VS1(H),VS2(H),V(H),DF(H),
DCL(H)
120 DIM XCL(H),XF(H),XH(H),CB(H),OH(H),II(H),CL(H),F(H),FM
(H)
130 DIM A(5),B(5),AA(5),BB(5),CC(5),MV(H),M(500),X(500),CL
M(H)
140 '
150 ' EXPLANATION OF VARIABLES
160 '
170 ' A = E0 OF ELECTRODE
180 ' AA = FIRST TERM OF CURVE FIT
190 ' B = SLOPE OF ELECTRODE
200 ' BB = SECOND TERM OF CURVE FIT
210 ' CB = CHARGE BALANCE
220 ' CC = THIRD TERM OF BEST FIT
230 ' CL = CHLORIDE ION CONCENTRATION
240 ' CLM = MOLES OF CHLORIDE
250 ' DCL = CHORIDE DISTRIBUTION COEFFICIENT
260 ' DF = FLUORIDE DISTRIBUTION COEFFICIENT
270 ' E1 = MV READING PH ELECTRODE
280 ' E2 = MV READING CL ELECTRODE
290 ' E3 = MV READING ELECTRODE 3
300 ' F = FLUORIDE ION CONCENTRATION
310 ' FM = MOLES OF FLUORIDE IN SOLUTION
320 ' G = ACTIVITY COEFFICIENT
330 ' H = HYDROGEN ION CONCENTRATION
```

```
340 ' II = IONIC STRENGTH
350 ' M = MV ASSUMED FOR CALCULATION
360 ' MV = MILLIVOLT READING
370 ' OH = OH ION CONCENTRATION
380 ' PCL = NEG LOG CHLORIDE ACTIVITY
390 ' PH = NEG LOG OF HYDROGRN ION ACT
400 ' PHCL = PH + PCL
410 ' PHF = PH + PF
420 ' PF = NEG LOG OF FLUORIDE ACTIVITY
430 ' V = TOTAL VOLUME
440 ' VA = VOLUME OF ACID
450 ' VB = VOLUME OF BASE
460 ' VS1 = VOLUME OF SALT
470 ' VS2 = VOLUME OF SALT 2
480 ' XCL = CHORIDE UPTAKE
490 ' XH = HYDROGEN UPTAKE
500 ' XF = FLUORIDE UPTAKE
510 ' X = COUNTER
520 ' XX = SUM OF CL + F UPTAKE
530 '
540 '
550 PRINT: PRINT: PRINT
560 PRINT: PRINT"THE FIRST ISE RECORDED MUST BE A pH ELECT
RODE"
570 PRINT"THE SECOND ISE RECORDED MUST BE A Cl ELECTRODE"
580 PRINT"ALSO, THE ADDED ACID, VA, WILL BE HYDROCHLORIC A
CID"
590 PRINT: INPUT"ENTER FILE NAME ";NM$
600 PRINT : INPUT "ENTER INITIAL IONIC STRENGTH " ;II0
610 '
620 '  INPUT DATA FROM FILE
630 '
640 '
650 INFILE$ = "\PROGRAMS\DATA\" + NM$
660 OPEN INFILE$ FOR INPUT AS #1
670 INPUT#1,N: INPUT#1,EO: INPUT#1,VO
680 INPUT#1,MB: INPUT#1,MS1: INPUT#1,MS2 : INPUT#1,MA
690 INPUT#1,GA: INPUT#1,GM
700 INPUT#1,NI
710 INPUT#1,A(1): INPUT#1,B(1): INPUT#1,A(2)
```

```
720 INPUT#1,B(2): INPUT#1,A(3): INPUT#1,B(3)
730 INPUT#1,AA(1): INPUT#1,BB(1): INPUT#1,CC(1)
740 INPUT#1,AA(2): INPUT#1,BB(2): INPUT#1,CC(2)
750 INPUT#1,AA(3): INPUT#1,BB(3): INPUT#1,CC(3)
760 FOR I = 1 TO N
770 INPUT#1,VB(I): INPUT#1,VS1(I): INPUT#1,VS2(I): INPUT#1
,VA(I):
780 INPUT#1,E1(I): INPUT#1,E2(I): INPUT#1,E3(I)
790 NEXT
800 CLOSE #1
810 PRINT
820 GOTO 880    ' SKIP SUBROUTINE FOR ACT COEFF CALC
830 '
840 ' DAVIS EQUATION FOR CALCULATION OF ACTIVITY COEFFICIE
NT
850 ' FROM IONIC STRENGTH
860 '
870 F = EXP (-1.1513 * (SQR(F)/(1 + SQR(F)) - .3 * F )) :
RETURN
880 '
890 PRINT:CLS
900 PRINT"DO YOU PREFER STRAIGHT LINE OR CURVE FIT ";
910 PRINT "DATA FOR YOUR CALIBRATION"
920 LOCATE 10,10 : INPUT"ENTER SL OR CF  ";D$
930 '
940 '
950 ' CALCULATE P VALUES USING ST LINE CALIBRATION DATA
960 '
970 '
980 FOR I = 1 TO N
990 ON NI GOTO 1020,1010,1000
1000 PF(I) =  ( E3(I) - A(3) ) / B(3)
1010 PCL(I) =  ( E2(I) - A(2) ) / B(2)
1020 PH(I) =  ( E1(I) - A(1) ) / B(1)
1030 NEXT
1040 '
1050 '
1060 IF (D$ = "SL")   OR  (D$ = "sl") GOTO 1730
1070 IF (D$ = "CF")   OR  (D$ = "cf") GOTO 1140
1080 GOTO 1060
```

```
1090 '
1100 '
1110 '  MATCH EACH ELECTRODE WITH THE CONSTANTS FOR ITS
1120 '  CURVE FIT EQUATION
1130 '
1140 FOR K = 1 TO NI
1150 ON K GOTO 1160,1200,1240
1160 AA = AA(1): BB = BB(1): CC = CC(1):
1170 FOR I = 1 TO N : MV(I) = E1(I) : NEXT  : GOSUB 1350
1180 GOTO 1260
1190 IF K = 2 GOTO 1200
1200 X = AC(I): AA = AA(2): BB = BB(2): CC = CC(2):
1210 FOR I = 1 TO N : MV(I) = E2(I) : NEXT  : GOSUB 1350
1220 GOTO 1260
1230 IF K = 3 GOTO 1240
1240 X = AI(I): AA = AA(3): BB = BB(3): CC = CC(3):
1250 FOR I = 1 TO N : MV(I) = E3(I) : NEXT  : GOSUB 1350
1260 NEXT
1270 GOTO 1790
1280 '
1290 '  SUBROUTINE FOR CALCULATING PH,PF,PCL USING CURVE F
IT
1300 ' FROM CALIBRATION DATA. A p VALUE IS ASSUMED AND A M
V VALUE
1310 '  IS CALCULATED. THIS IS REPEATED UNTIL THE CALCULAT
ED MV
1320 '  IS LESS THAN .01 MV DIFFERENT FROM THE MEASURED VA
LUE
1330 '
1340 '
1350 CLS : LOCATE 10,25 : PRINT "**********************
**"
1360 FOR I = 1 TO N
1370 LOCATE 9,25 : PRINT " CALCULATIONS IN PROGRESS"
1380 ON K GOTO 1390,1400,1410
1390 X(1) = PH(I) : GOTO 1420
1400 X(1) = PCL(I)  : GOTO 1420
1410 X(1) = PF(I)  : GOTO 1420
1420 T=1 : TB = 0
1430 T = T + 1
```

```
1440 TB = TB + 1
1450 M(T) = AA + BB * X(TB)+ CC * X(TB) ^ 2
1460 IF ABS(M(T) - MV(I) )  < .001 THEN GOTO 1650
1470 LOCATE 15,20 : PRINT "M(T)="M(T),"MV(I)="MV(I),I
1480 '
1490 '
1500 IF M(T) = > MV(I) THEN XH = X(TB)
1510 IF M(T) = < MV(I) THEN XL = X(TB)
1520 '
1530 '
1540 IF TB < 2.1 GOTO 1590
1550 IF X(TB) = XH THEN X(TB + 1) = (XH + XL ) / 2 : GOTO
1430
1560 IF X(TB) = XL THEN X(TB + 1) = (XH + XL ) / 2 : GOTO
1430
1570 '
1580 '
1590 IF X(TB) = XH THEN IF BB> 0 THEN X(TB + 1) = .5*X(TB)
 :           GOTO 1430
1600 IF X(TB) = XH THEN IF BB< 0 THEN X(TB + 1) = 2*X(TB)
:           GOTO 1430
1610 IF X(TB) = XL THEN IF BB> 0 THEN X(TB + 1) = 2*X(TB)
:           GOTO 1430
1620 IF X(TB) = XL THEN IF BB< 0 THEN X(TB + 1) =.5*X(TB)
:           GOTO 1430
1630 '
1640 '
1650 ON K GOTO 1680,1670,1660
1660 PF(I) = X(TB) : GOTO 1690
1670 PCL(I) = X(TB) : GOTO 1690
1680 PH(I) = X(TB) : GOTO 1690
1690 NEXT
1700 RETURN
1710 '
1720 '
1730 CLS : LOCATE 10,10
1740 INPUT "DO YOU WANT SCREEN PRINT OF RESULTS  Y/N ";SK$
1750 IF (SK$ = "N") OR (SK$ = "n") GOTO 1780
1760 IF (SK$ = "Y") OR (SK$ = "y") GOTO 1800
1770 GOTO 1740
```

```
1780 CLS
1790 LOCATE 15,30 : PRINT "CALCULATIONS IN PROGRESS"
1800 FOR I = 1 TO N
1810 '
1820 '
1830 'DISPLAYS NO. OF DATA POINT BEING PROCESSED
1840 '
1850 IF (SK$ = "y") OR (SK$ = "Y") GOTO 1920
1860 LOCATE 15,25 : PRINT I
1870 '
1880 '
1890 ' IONIC STRENTH AND ACTIVITY COEFFICIENT CALCULATIONS
1900 '
1910 '
1920 '  MMOLES OF SALTS ADDED
1930 '
1940 '
1950 ACID = VA(I) * MA
1960 BASE = VB(I) * MB
1970 S1 = VS1(I) * MS1
1980 S2 = VS2(I) * MS2
1990 '
2000 '
2010 '
2020 G(I) = 1
2030 V(I) = VO + VB(I) + VS1(I) + VS2(I) +VA(I)
2040 '
2050 '
2060 ' CHANGE P VALUES INTO CONCENTRATION USING
2070 ' CONCENTRATION = ACTIVITY / ACTIVITY COEFFICIENT
2080 '
2090 ON NI GOTO 2120,2110,2100
2100 F(I) = EXP (-PF(I) *2.302585) / G(I)
2110 CL(I) = EXP (-PCL(I) * 2.302585) / G(I)
2120 H(I) = EXP (-PH(I) * 2.302585) / G(I)
2130 '
2140 OH(I) = 1E-14 / (H(I) * G(I) ^ 2)
2150 IF NI = 1 THEN GOTO 2200
2160 '
2170 II(I) = CL(I) + F(I) + OH(I) + II0 : GOTO 2220
```

```
2180 '  USE OF ISOELECTRIC POINT TO CALCULATE IONIC STRENG
TH
2190 '
2200 IF PH(I)> EO THEN S = S1 + S2 + ACID ELSE S = S1 + S2
 + BASE
2210 II(I) = S / V(I) + OH(I) + H(I)
2220 F = II(I): GOSUB 870: Y = F
2230 IF G(I) / Y < 1.0001 THEN 2290
2240 G(I) = Y
2250 GOTO 2030
2260 '
2270 '
2280 '
2290 ' PA FOR EACH SALT
2300 '
2310 PHCL(I) =  PCL(I) + PH(I)
2320 PHF(I) =  PF(I) + PH(I)
2330 '
2340 '
2350 '
2360 ' MMOLES OF EACH SALT MEASURED
2370 '
2380 H(I) = H(I) * V(I)
2390 CLM(I) = CL(I) * V(I)
2400 FM(I) = F(I) * V(I)
2410 OH(I) = OH(I) * V(I)
2420 '
2430 '
2440 '
2450 '  UPTAKE OF EACH SALT
2460 '
2470 XCL(I) = ( CLM(I) -  (ACID + CLM(1) + S1) )/ GM
2480 '
2490 'XCL = (MOLES OF CL MEASURED  - ( INITIAL CL + HCL AD
DED
2500 ' + MOLES OF CL ADDED ) / GRMS OF EXCHANGER = CL / GM
2510 '
2520 XF(I) = ( FM(I) - S2 )  / GM
2530 '
2540 'XF = ( MOLES OF F MEASURED - MOLES OF F ADDED ) /
```

```
2550 ' GRMS OF EXCHANGER  = UPTAKE F / GM
2560 '
2570 XH(I) = ( BASE - ACID  + H(I) - OH(I) - H(1) ) / GM
2580 '
2590 ' XH = ( MOLES OF BASE ADDED - MOLES OF ACID ADDED
2600 '  + (H+) MEASURED - OH MEASURED - INITIAL (H+) ) / G
RMS OF EXCHANGER
2610 '       =  CHANGE IN (H+) UPTAKE / GM
2620 '
2630 CB(I) = ( XCL(I) + XF(I) - XH(I) )
2640 XX(I) = (  XCL(I) + XF(I)  )
2650 '
2660 '
2670 '   DITRIBUTION COEFFI CIENT
2680 '
2685 ON NI GOTO 2710,2700,2690
2690 DF(I) = XF(I) / F(I)
2700 DCL(I) = XCL(I) / CL(I)
2710 '
2720 IF (SK$ = "N") OR (SK$ = "n") GOTO 2930
2730 PRINT: PRINT: PRINT
2740 PRINT " N = ";I : PRINT
2750 PRINT " PH = "; PH(I)
2760 PRINT "ACTIVITY COEFFICIENT = ";G(I)
2770 PRINT "IONIC STRENGTH = ";II(I)
2780 PRINT "MMOLES CHLORIDE = ";CLM(I)
2790 PRINT "MMOLES ISE NO.3 = ";FM(I)
2800 PRINT "MMOLES H        = ";H(I)
2810 PRINT "MMOLES OH       = ";OH(I)
2820 PRINT "MMOLES A        = ";ACID
2830 PRINT "MMOLES B        = ";BASE
2840 PRINT "PCL             = ";PCL(I)
2850 PRINT "PHCL            = ";PHCL(I)
2860 PRINT "PF              = ";PF(I)
2870 PRINT "PHF            = ";PHF(I)
2880 PRINT "UPTAKE CHLORIDE =";XCL(I)
2890 PRINT "UPTAKE ION NO.3 =";XF(I)
2900 PRINT "UPTAKE H        = ";XH(I)
2910 PRINT "ANION BALANCE   =";XX(I)
2920 PRINT "CHARGE BALANCE  =";CB(I)
```

```
2930 NEXT
2940 PRINT
2950 '
2960 '
2970 ' WRITE RESULTS TO FILE
2980 '
2990 '
3000 INFILE$ = "\PROGRAMS\DATA\RESULTS\" + NM$
3010 OPEN INFILE$ FOR OUTPUT AS #1
3020 WRITE#1,N: WRITE#1,EO: WRITE#1,VO
3030 WRITE#1,MB: WRITE#1,MS1: WRITE#1,MS2: WRITE#1,MA
3040 WRITE#1,GA: WRITE#1,GM: WRITE#1,NI
3050 FOR I = 1 TO N: WRITE#1,VB(I): NEXT
3060 FOR I = 1 TO N: WRITE#1,VS1(I): NEXT
3070 FOR I = 1 TO N: WRITE#1,VS2(I): NEXT
3080 FOR I = 1 TO N: WRITE#1,VA(I): NEXT
3090 FOR I = 1 TO N: WRITE#1,PH(I): NEXT
3100 FOR I = 1 TO N: WRITE#1,CLM(I): NEXT
3110 FOR I = 1 TO N: WRITE#1,FM(I): NEXT
3120 FOR I = 1 TO N: WRITE#1,XH(I): NEXT
3130 FOR I = 1 TO N: WRITE#1,XCL(I): NEXT
3140 FOR I = 1 TO N: WRITE#1,XF(I): NEXT
3150 FOR I = 1 TO N: WRITE#1,CB(I): NEXT
3160 FOR I = 1 TO N: WRITE#1,PHCL(I): NEXT
3170 FOR I = 1 TO N: WRITE#1,PHF(I): NEXT
3180 FOR I = 1 TO N: WRITE#1,XX(I): NEXT
3190 FOR I = 1 TO N: WRITE#1,II(I): NEXT
3200 FOR I = 1 TO N: WRITE#1,G(I): NEXT
3210 FOR I = 1 TO N: WRITE#1,DCL(I): NEXT
3220 FOR I = 1 TO N: WRITE#1,DF(I): NEXT
3230 FOR I = 1 TO N: WRITE#1,CL(I): NEXT
3240 FOR I = 1 TO N: WRITE#1,F(I): NEXT
3250 CLOSE #1
3260 CLS
3270 END
```

APPENDIX P4.5 PRINT RESULTS PROGRAM

```
10 ' PR5 UPDATED 7-4-87
20 ' PRINT RESULTS REV 5 PROGRAM
30 H = 40
40 DIM VB(H),VS1(H),VS2(H),VS3(H),VA(H),PH(H),CL(H),C3(H),
XH(H),CB(H)
50 DIM PCL(H),PC3(H),XX(H),PA2(H),PA3(H),XCL(H),X3(H),II(H
),G(H)
60 DIM CLM(H),C3M(H),DCL(H),DC3(H)
70 CLS
80 PRINT: INPUT"ENTER FILE NAME ";NM$
90 INFILE$ = "\PROGRAMS\DATA\RESULTS\" + NM$
100 OPEN INFILE$ FOR INPUT AS #1
110 INPUT#1,N: INPUT#1,EO: INPUT#1,VO
120 INPUT#1,MB: INPUT#1,MS1: INPUT#1,MS2: INPUT#1,MA
130 INPUT#1,GA: INPUT#1,GM: INPUT#1,NI
140 FOR I = 1 TO N: INPUT#1,VB(I): NEXT
150 FOR I = 1 TO N: INPUT#1,VS1(I): NEXT
160 FOR I = 1 TO N: INPUT#1,VS2(I): NEXT
170 FOR I = 1 TO N: INPUT#1,VA(I): NEXT
180 FOR I = 1 TO N: INPUT#1,PH(I): NEXT
190 FOR I = 1 TO N: INPUT#1,CLM(I): NEXT
200 FOR I = 1 TO N: INPUT#1,C3M(I): NEXT
210 FOR I = 1 TO N: INPUT#1,XH(I): NEXT
220 FOR I = 1 TO N: INPUT#1,XCL(I): NEXT
230 FOR I = 1 TO N: INPUT#1,X3(I): NEXT
240 FOR I = 1 TO N: INPUT#1,CB(I): NEXT
250 FOR I = 1 TO N: INPUT#1,PA2(I): NEXT
260 FOR I = 1 TO N: INPUT#1,PA3(I): NEXT
270 FOR I = 1 TO N: INPUT#1,XX(I): NEXT
280 FOR I = 1 TO N: INPUT#1,II(I): NEXT
290 FOR I = 1 TO N: INPUT#1,G(I): NEXT
300 FOR I = 1 TO N: INPUT#1,DCL(I): NEXT
310 FOR I = 1 TO N: INPUT#1,DC3(I): NEXT
320 FOR I = 1 TO N: INPUT#1,CL(I): NEXT
330 FOR I = 1 TO N: INPUT#1,C3(I): NEXT
340 CLOSE #1
```

```
350 CLS
360 PRINT: INPUT"ENTER NAME OF UPTAKE PROGRAM USED ";UP$
370 PRINT: INPUT"ENTER NAME OF ISE NO.1 ";N1$
380 IF NI = 1 GOTO 420
390 PRINT: INPUT"ENTER NAME OF ISE NO.2 ";N2$
400 IF NI = 2 GOTO 420
410 PRINT: INPUT"ENTER NAME OF ISE NO.3 ";N3$
420 CLS
430 PRINT : PRINT : INPUT " DO YOU WANT SCREEN PRINT Y/N "
;SP$
440 IF (SP$ = "Y") OR (SP$ = "y") THEN GOTO 470
450 IF (SP$ = "N") OR (SP$ = "n") THEN GOTO 1350
460 GOTO 430
470 PRINT: PRINT "FILE NAME",TAB(30)NM$
480 PRINT "NO. OF DATA SETS",TAB(30)N
490 PRINT "ISOELECTRIC POINT",TAB(30)EO
500 PRINT "INITIAL VOLUME",TAB(30)VO
510 PRINT "MOLARITY OF BASE",TAB(30)MB
520 PRINT "MOLARITY OF SALT 1 ",TAB(30)MS1
530 PRINT "MOLARITY OF SALT 2 ",TAB(30)MS2
540 PRINT "MOLARITY OF ACID",TAB(30)MA
550 PRINT "GRAMS OF EXCHANGER",TAB(30)GA
560 PRINT "GRAMS DRIED EXCHANGER",TAB(30)GM
570 IF NI = 1 GOTO 610
580 PRINT "CL = CONC. APPARENT FROM "TAB(26)N2$" ELECTRODE
"
590 IF NI = 2 GOTO 610
600 PRINT "C3 = CONC. APPARENT FROM "TAB(26)N3$" ELECTRODE
"
610 PRINT "II = IONIC STRENGTH"
620 PRINT "ACT = ACTIVITY COEFFICIENT"
630 PRINT "UPTAKE PROGRAM USED IS "TAB(24)UP$
640 PRINT: PRINT: PRINT
650 PRINT TAB(2)"VB" TAB(8)"VS1" TAB(14)"VS2" TAB(20)"VA"
TAB(28)"PH" TAB(37)"CL
" TAB(46);
660 IF (NI = 1) OR (NI = 2) GOTO 680
670 PRINT "C3" TAB(55);
680 PRINT TAB(58)"II";
690  PRINT TAB(70)"ACT"
```

```
700 FOR I = 1 TO N
710 PRINT TAB(2)VB(I) TAB(8)VS1(I) TAB(14);
720 PRINT USING"##.#";VS2(I);
730 PRINT TAB(20);
740 PRINT USING"##.##";VA(I);
750 PRINT TAB(28);
760 PRINT USING"##.###";PH(I);
770 PRINT TAB(37);
780 PRINT USING"#.##^^^^";CL(I);
790 PRINT TAB(46);
800 IF (NI = 1) OR (NI = 2) GOTO 820
810 PRINT USING"#.##^^^^";C3(I);
820 PRINT TAB(55);
830 PRINT USING"#.####^^^^";II(I);
840 PRINT TAB(70);
850 PRINT USING "#.###";G(I)
860 NEXT
870 CLS
880 PRINT"FILE NAME = "NM$
890 PRINT"XH = UPTAKE OF "TAB(16)N1$" IN MMOLE/GRAM EXCHAN
GER"
900 IF NI = 1 GOTO 940
910 PRINT"XCL = UPTAKE OF "TAB(17)N2$" IN MMOLE/GRAM EXCHA
NGER"
920 IF NI = 2 GOTO 940
930 PRINT"X3 = UPTAKE OF "TAB(16)N3$" IN MMOLE/GRAM EXCHAN
GER"
940 PRINT"CB = CHARGE BALANCE,ANIONS VS CATIONS"
950 PRINT"XX = ANION BALANCE"
960 PRINT"DCL = CL DISTRIBUTION COEFFICIENT"
970 IF (NI = 1) OR (NI = 2) GOTO 990
980 PRINT"DC3 = ION 3 DISTRIBUTION COEFFICIENT"
990 PRINT: PRINT: PRINT
1000 PRINT TAB(1);
1010 PRINT "XH" TAB(7);
1020 IF (NI = 1) OR (NI = 2) GOTO 1050
1030 PRINT "XCL" TAB(14);
1040 PRINT "X3";
1050 PRINT TAB(21)"CB" TAB(28)"XX" TAB(35)"PA2";
1060 IF (NI = 1) OR (NI = 2) GOTO 1090
```

```
1070 PRINT TAB(42);
1080 PRINT "PA3";
1090 PRINT TAB(51)"DCL"TAB(59);
1100 IF (NI = 1) OR (NI = 2) GOTO 1120
1110 PRINT "DC3"
1120 FOR I = 1 TO N
1130 PRINT TAB(1);
1140 PRINT USING"##.###";XH(I);
1150 PRINT TAB(7);
1160 IF (NI - 1) OR (NI - 2) GOTO 1200
1170 PRINT USING"##.###";XCL(I);
1180 PRINT TAB(14);
1190 PRINT USING"##.###";X3(I);
1200 PRINT TAB(21);
1210 PRINT USING"##.###";CB(I);
1220 PRINT TAB(28);
1230 PRINT USING"##.###";XX(I);
1240 PRINT TAB(35);
1250 PRINT USING"##.###";PA2(I);
1260 IF (NI = 1) OR (NI = 2) GOTO 1290
1270 PRINT TAB(42);
1280 PRINT USING"##.###";PA3(I)
1290 PRINT TAB(51);
1300 PRINT USING"######";DCL(I);
1310 PRINT TAB(59);
1320 IF (NI = 1) OR (NI =2) GOTO 1340
1330 PRINT USING"######";DC3(I)
1340 NEXT
1350 PRINT : PRINT : INPUT " DO YOU WANT A HARD COPY Y/N "
;HC$
1360 IF (HC$ = "Y") OR (HC$ = "y") THEN GOTO 1390
1370 IF (HC$ = "N") OR (HC$ = "n") THEN GOTO 2410
1380 GOTO 1350
1390 LPRINT: LPRINT "FILE NAME",TAB(30)NM$
1400 LPRINT "NO. OF DATA SETS",TAB(30)N
1410 LPRINT "ISOELECTRIC POINT",TAB(30)EO
1420 LPRINT "INITIAL VOLUME",TAB(30)VO
1430 LPRINT "MOLARITY OF BASE",TAB(30)MB
1440 LPRINT "MOLARITY OF SALT 1 ",TAB(30)MS1
1450 LPRINT "MOLARITY OF SALT 2 ",TAB(30)MS2
```

```
1460 LPRINT "MOLARITY OF ACID",TAB(30)MA
1470 LPRINT "GRAMS OF EXCHANGER",TAB(30)GA
1480 LPRINT "GRAMS DRIED EXCHANGER",TAB(30)GM
1490 IF NI = 1 GOTO 1510
1500 GOTO 1520
1510 LPRINT "CL = CONC. APPARENT FROM ADDED CL SALT ,IF AN
Y, AND PH ELECTRODE"
1520 IF NI = 1 GOTO 1560
1530 LPRINT "CL = CONC. APPARENT FROM "TAB(26)N2$" ELECTRO
DE"
1540 IF NI = 2 GOTO 1560
1550 LPRINT "C3 = CONC. APPARENT FROM "TAB(26)N3$" ELECTRO
DE"
1560 LPRINT "II = IONIC STRENGTH"
1570 LPRINT "ACT = ACTIVITY COEFFICIENT"
1580 LPRINT "UPTAKE PROGRAM USED IS "TAB(24)UP$
1590 LPRINT: LPRINT: LPRINT
1600 LPRINT TAB(1)"N" TAB(6)"VB" TAB(12)"VS1" TAB(18)"VS2"
 TAB(25)"VA" TAB(33)"P
H" TAB(41)"CL" TAB(52);
1610 IF (NI = 1) OR (NI = 2) GOTO 1630
1620 LPRINT "C3" ;
1630 LPRINT TAB(60);
1640 LPRINT "II";
1650 LPRINT TAB(72);
1660 LPRINT "ACT"
1670 LPRINT
1680 FOR I = 1 TO N
1690 LPRINT I TAB(5)VB(I) TAB(11)VS1(I) TAB(17);
1700 LPRINT USING"##.#";VS2(I);
1710 LPRINT TAB(23);
1720 LPRINT USING"##.##";VA(I);
1730 LPRINT TAB(30);
1740 LPRINT USING"##.###";PH(I);
1750 LPRINT TAB(38);
1760 LPRINT USING"#.##^^^^";CL(I);
1770 IF (NI = 1) OR (NI = 2) GOTO 1800
1780 LPRINT TAB(48);
1790 LPRINT USING"#.##^^^^";C3(I);
1800 LPRINT TAB(59);
```

```
1810 LPRINT USING"#:####^^^^";II(I);
1820 LPRINT TAB(73);
1830 LPRINT USING"#.###";G(I)
1840 NEXT
1850 LPRINT CHR$(12)
1860 LPRINT"FILE NAME = "NM$
1870 LPRINT"XH = UPTAKE OF "TAB(16)N1$" IN MMOLE/GRAM EXCH
ANGER"
1875 IF NI = 1 GOTO 1880
1877 GOTO 1885
1880 LPRINT"XCL = UPTAKE OF CL(FROM PH ELECTRODE) IN MMOLE
/GRAM EXCHANGER"
1885 IF (NI = 1) OR (NI = 2) GOTO 1920
1890 LPRINT"XCL = UPTAKE OF "TAB(17)N2$" IN MMOLE/GRAM EXC
HANGER"
1900 IF NI = 2 GOTO 1920
1910 LPRINT"X3 = UPTAKE OF "TAB(16)N3$" IN MMOLE/GRAM EXCH
ANGER"
1920 LPRINT"CB = CHARGE BALANCE,ANIONS VS CATIONS"
1930 LPRINT"XX = ANION BALANCE"
1940 LPRINT"PA2 = PH + PCL"
1950 IF (NI = 1) OR (NI =2) GOTO 1970
1960 LPRINT"PA3 = PH + P(ISE NO.3)"
1970 LPRINT"DCL = CL DISTRIBUTION COEFFICIENT"
1980 IF (NI = 1) OR (NI = 2) GOTO 2000
1990 LPRINT"DC3 = ION 3 DISTRIBUTION COEFFICIENT"
2000 LPRINT: LPRINT: LPRINT
2010 LPRINT TAB(1)"N";
2020 LPRINT TAB(7);
2030 LPRINT "XH" TAB(15);
2050 LPRINT "XCL" TAB(22);
2060 IF (NI =1) OR (NI = 2) GOTO 2080
2070 LPRINT "X3";
2080 LPRINT TAB(30)"CB" TAB(36)"XX" TAB(43)"PA2";
2090 IF (NI = 1) OR (NI = 2) GOTO 2120
2100 LPRINT TAB(49);
2110 LPRINT "PA3";
2120 LPRINT TAB(58)"DCL";
2130 IF (NI = 1) OR (NI =2) GOTO 2150
2140 LPRINT TAB(64)"DC3"
```

```
2150 FOR I = 1 TO N
2160 LPRINT TAB(1)I;
2170 LPRINT TAB(6);
2180 LPRINT USING"##.###";XH(I);
2190 LPRINT TAB(13);
2210 LPRINT USING"##.###";XCL(I);
2220 LPRINT TAB(21);
2230 IF (NI = 1) OR (NI = 2) GOTO 2250
2240 LPRINT USING"##.###";X3(I);
2250 LPRINT TAB(27);
2260 LPRINT USING"##.###";CB(I);
2270 LPRINT TAB(34);
2280 LPRINT USING"##.###";XX(I);
2290 LPRINT TAB(41);
2300 LPRINT USING"##.###";PA2(I);
2310 IF (NI = 1) OR (NI = 2) GOTO 2340
2320 LPRINT TAB(48);
2330 LPRINT USING"##.###";PA3(I);
2340 LPRINT TAB(55);
2350 LPRINT USING"######";DCL(I);
2360 IF (NI = 1) OR (NI = 2) GOTO 2390
2370 LPRINT TAB(62);
2380 LPRINT USING"######";DC3(I)
2390 NEXT
2400 LPRINT CHR$(12)
2410 END
```

APPENDIX P4.6 MULTIPLOT PROGRAM

```
10 'SCREEN MULTIPLOT  September 27, 1986
20 'FILENAME PLT4.BAS
30 H = 80
40 CLS
50 DIM PH(H),XX(H),ML(H),PA(H),PB(H),MA(H),C(H),YT(H),XT(H
),CB(H),II(H)
60 DIM VB(H),VA(H),VS1(H),VS2(H),CLM(H),C3M(H),XCL(H),X3(H
),CL(H),C3(H),XF(H)
70 DIM XH(H),XOH(H),PHCL(H),PHF(H),XAP(H),YAP(H),G(H),DCL(
H),D3(H),BT(H)
80 LOCATE 10,30 : PRINT  " WELCOME TO MULTIPLOT "
100 LOCATE 19,1 : INPUT "NUMBER OF FILES  ";NF
110 FOR I = 1 TO NF
120 PRINT:PRINT:PRINT "FILE";I;SPC(10)
130 INPUT "NAME OF FILE ";D$(I)
140 NEXT
150 '
160 CLS
170 PRINT: PRINT TAB(10) "THIS FILE CONTAINS THE FOLLOWING
 PARAMETERS"
180 PRINT : PRINT TAB(5) "VOLUME OF BASE                VB"
190 PRINT TAB(5) "VOLUME OF SALT 1              VS1"
200 PRINT TAB(5) "VOLUME OF SALT 2              VS2"
210 PRINT TAB(5) "VOLUME OF ACID                VA"
220 PRINT TAB(5) "PH                            PH"
230 PRINT TAB(5) "PCL                           PCL"
240 PRINT TAB(5) "PF                            PF"
250 PRINT TAB(5) "PHCL                          PHCL"
260 PRINT TAB(5) "PHF                           PHF"
270 PRINT TAB(5) "MOLES OF CHLORIDE             CLM"
280 PRINT TAB(5) "MOLES OF FLUORIDE             FM"
290 PRINT TAB(5) "PROTON UPTAKE                 XH"
300 PRINT TAB(5) "CHLORIDE UPTAKE               XCL"
310 PRINT TAB(5) "FLUORIDE UPTAKE               XF"
320 PRINT TAB(5) "DISTRIBUTION COEFFICENT CL    DCL"
330 PRINT TAB(5) "DISTRIBUTION COEFFICENT F     DF"
```

```
340 PRINT TAB(5) "CHARGE BALANCE                    CB"
350 '
360 '
370 PRINT : INPUT "X AXIS = ";XT$
380 PRINT : INPUT "Y AXIS = ";YT$
390 '
400 PRINT : INPUT "CONNECT POINTS Y/N ";LN$
410 CLS
420 LOCATE 10,30 : INPUT "CALCULATE MAX MIN  Y/N ";CMM$
422 IF (CMM$ = "Y") OR (CMM$ = "y") THEN GOTO 650
424 IF (CMM$ = "N") OR (CMM$ = "n") THEN GOTO 500
426 GOTO 420
430 '
440 '
460 '
470 '
480 '       SUBROUTINE FOR INPUTTING MAX AND MIN VALUES
490 '
500 PRINT:PRINT:PRINT "TITLE OF X AXIS IS  ";XT$
510 PRINT : PRINT SPC(25) XT$ ;
520 INPUT " MIN  ";XMIN
530 PRINT: PRINT SPC(25) XT$ ;
540 INPUT " MAX  ";XMAX
550 PRINT:PRINT:PRINT "TITLE OF Y AXIS IS  ";YT$
560 PRINT: PRINT SPC(25) YT$ ;
570 INPUT " MIN  ";YMIN
580 PRINT: PRINT SPC(25) YT$ ;
590 INPUT " MAX  ";YMAX
600 GOTO 1240
610 '
620 '
630 '     SUBROUTINE  TO DETERMINE MAX AND MIN VALUES  THR
U LINE 1100
640 '
650 CLS : LOCATE 10,10 : PRINT "CALCULATING MAX AND MIN VA
LUES"
660 FOR T = 1 TO NF
670 GOSUB 2970
680 BT$ = XT$ : GOSUB 3230 : FOR I = 1 TO N : XT(I) = BT(I
) : NEXT
```

```
690 BT$= YT$ : GOSUB 3230 : FOR I = 1 TO N : YT(I) = BT(I)
 : NEXT
700 '
710 '
720 '
730 '
740 '   XMIN
750 '
760 IF T = 1 THEN  XMIN = XT(1) : GOTO 780
770 IF T > 1  THEN  IF XMIN < XT(1) THEN GOTO 780  ELSE XM
IN = XT(1)
780 FOR K = 2 TO N
790 IF XMIN < XT(K) GOTO 810
800 LET XMIN = XT(K)
810 NEXT K
820 '
830 '  XMAX
840 '
850 IF T = 1 THEN XMAX = XT(1) : GOTO 870
860 IF T > 1 THEN IF XMAX > XT(1) THEN GOTO 870 ELSE XMAX
= XT(1)
870 FOR K = 2 TO N
880 IF XMAX > XT(K) GOTO  900
890 XMAX = XT(K)
900 NEXT K
910 '
920 '  YMIN
930 '
940 IF T = 1 THEN YMIN = YT(1) : GOTO 960
950 IF T > 1 THEN IF YMIN < YT(1) GOTO 960 ELSE YMIN = YT(
1)
960 FOR K = 2 TO N
970 IF YMIN < YT(K) GOTO 990
980 LET YMIN = YT(K)
990 NEXT K
1000 '
1010 '  YMAX
1020 '
1030 IF T = 1 THEN YMAX = YT(1) : GOTO 1050
1040 IF T > 1 THEN IF YMAX > YT(1) GOTO 1050 ELSE YMAX = Y
```

```
T(1)
1050 FOR K = 2 TO N
1060 IF YMAX > YT(K) GOTO  1080
1070 YMAX = YT(K)
1080 NEXT K
1090 NEXT T
1100 CLS
1110 '
1120  PRINT "XMIN = "XMIN
1130  PRINT "XMAX = "XMAX
1140  PRINT "YMIN = "YMIN
1150  PRINT "YMAX = "YMAX
1160 '
1170  PRINT : PRINT : INPUT "USE CALCULATED MAX MIN  Y/N";
MN$
1180  IF (MN$ = "Y") OR (MN$ = "y") THEN GOTO 1220
1190  IF (MN$ = "N") OR (MN$ = "n") THEN GOTO 480
1200  GOTO 1170
1210 '
1220 '          SUBROUTINE TO DRAW BOX
1230 '
1240 GX = 9 : GY = 10
1250 CLS
1260 LINE (220,1)-(580,160),,B        'DRAWS BOX
1270 LINE (219,1)-(219,160)           'FILLS IN VERTICAL LI
NES
1280 LINE (581,1)-(581,160)           'FILLS IN VERTICAL LI
NES
1290 '
1300 '
1310 ' SUBROUTINE FOR X GRATICES
1320 '
1330 B = 360 / GX                      'DEFINES SPACE BETWE
EN EACH X GRATICES
1340 FOR I = 1 TO GX-1
1350 BX = 220 + (B * I)                'DEFINES X POSITION
OF EACH X GRATICES
1360 LINE (BX,160)-(BX,160-10)         'DRAWS A LINE FOR EA
CH X GRATICES
1370 LINE (BX-1,160)-(BX-1,160-10)     'FILLS IN THE X GRAT
```

```
ICES
1380 NEXT
1390 '
1400 '
1410 ' SUBROUTINE FOR VALUES OF X GRATICES
1420 '
1430 D = (XMAX -XMIN) / GX              'DEFINES DELTA VALUE
 FOR EACH X GRATICES
1440 BNX = 45 / GX                     'DEFINES NUMBER OF C
HARACTER LINES BETWEEN
                                        EACH X GRATICES
1450 FOR I = 1 TO GX - 1
1460 X = 26 + ( BNX * I )              'DEFINES X CHARATER
POSTION OF X VALUES
1470 Y = 22                            'DEFINES Y POSITION
OF X GRATICES VALUES
1480 C = XMIN + (D * I)                 'DEFINES VALUE OF
EACH X GRATICES
1490 IF OA = 2 GOTO 1520
1500 LOCATE Y,X : PRINT USING "##.#";C
1510 GOTO 1530
1520 LOCATE Y,X : PRINT USING "#.##";C
1530 NEXT
1540 LOCATE 24,52 : PRINT XT$          'LABELS X AXIS
1550 '
1560 '
1570 ' SUBROUTINE FOR Y GRATICES
1580 '
1590 E = 160 / GY                       'DEFINES SPACE BETW
EEN EACH Y GRATICES
1600 FOR I = 1 TO GY-1
1610 EY = 160 - ( E * I )               'DEFINES Y POSTION
OF EACH Y GRATICES
1620 '
1630 LINE (220,EY)-(220+25,EY)          'DRAWS A LINE FOR E
ACH Y GRATICES
1640 NEXT
1650 '
1660 '
1670 ' SUBROUTINE FOR VALUES OF Y GRATICES
```

```
1680 H = (YMAX-YMIN) / GY                    'DEFINES DELTA VAL
UE FOR EACH Y GRATICES
1690 ENY = 20/GY                           'DEFINES NUMBER OF CH
ARACTER LINES BETWEEN
                                            EACH Y GRATICES
1700 FOR I = 1 TO GY - 1
1710 Y = 20 - (ENY * I)                     'DEFINES Y CHARACTE
R POSITION OF EACH Y
                                             GRATICES
1720 X = 22                                'DEFINES X CHARACTER
 POSITON OF Y GRATICES
1730 F = YMIN + (H * I)                      'DEFINES ABSOLUTE
 VALUE OF Y GRATICES
1740 LOCATE Y,X : PRINT USING "##.##";F
1750 NEXT
1760 LOCATE 10,17 : PRINT YT$              'LABELS Y AXIS
1770 LOCATE 24,1
1780 '
1790 ' SUBROUTINE FOR INPUTTNG DATA FROM FILE
1800 '
1810 FOR T = 1 TO NF
1820 GOSUB 2970
1830 BT$ = XT$ : GOSUB 3230 : FOR I = 1 TO N : XT(I) = BT(
I) : NEXT
1840 BT$ = YT$ : GOSUB 3230 : FOR I = 1 TO N : YT(I) = BT(
I) : NEXT
1850 FOR J = 1 TO N
1861 XQ = (XT(J) - XMIN) / (XMAX - XMIN) 'PROPORTIONAL DIS
TANCE OF X ON X AXIS
1870 YQ = (YT(J) - YMIN) / (YMAX - YMIN) 'PROPORTIONAL DIS
TANCE OF Y ON Y AXIS
1880 DX = 360 : DY = 160                  'LENGTH OF X AND Y AX
IS IN PIXELS
1890 XP = XQ * DX                          'ABSOLUTE DISTANCE O
F X ON X AXIS
1900 YP = YQ * DY                          'ABSOLUTE DISTANCE O
F Y ON Y AXIS
1910 NC = T
1920 XAP(J) = 220 + XP                       'ABSOLUTE LOCATI
ON OF X ON THE SCREEN
```

```
1930 YAP(J) = 160 - YP                          'ABSOLUTE LOCATI
ON OF Y ON THE SCREEN
1935 IF (XAP(J) > 580) OR (XAP(J) < 220) OR (YAP(J) > 160)
 THEN GOTO 2050
1940 IF (AO$ = "Y") OR (AO$ = "y") THEN IF W = 1 THEN  IF
T = 1 THEN GOTO 2040
1950 IF (AO$ = "Y") OR (AO$ = "y") THEN IF W = 1 THEN  IF
T = 2 THEN GOTO 2020
1960 IF (AO$ = "Y") OR (AO$ = "y") THEN IF W = 2 THEN  IF
T = 1 THEN GOTO 2020
1970 IF (AO$ = "Y") OR (AO$ = "y") THEN IF W = 2 THEN  IF
T = 2 THEN GOTO 2040
1980 ON T GOTO 1990,2000,2010,2020,2030,2040
1990 GOSUB 2100 : GOTO 2050
2000 GOSUB 2280 : GOTO 2050
2010 GOSUB 2420 : GOTO 2050
2020 NC = 3 : GOSUB 2120 : GOTO 2050
2030 NC = 1 : GOSUB 2280 : GOTO 2050
2040 NC = 2 : GOSUB 2420 : GOTO 2050
2050 NEXT J
2060 GOSUB 2520
2070 NEXT T
2080 GOTO  2690
2090 '
2100 'SUBROUTINE FOR DRAWING CIRCLES
2110 '
2120 PRESET(XAP(J),YAP(J)),NC                   'DISPLAYS PIXE
L OF X,Y COORDINATES
                                                 ON THE SCREEN
,COLOR 1
2130 CIRCLE(XAP(J),YAP(J)),5,NC                 'DRAWS CIRCLE
OF 5 PIXEL RADIUS
                                                 ON THE SCREEN
,COLOR 1
2140 '
2150 IF (LN$ = "Y") OR (LN$ = "y") THEN GOSUB 2210
2160 RETURN
2170 '
2180 '
2190 '    SUBROUTINE TO CONNECT THE POINTS
```

```
2200 '
2210 IF (J - 1) OR  (LNS - 1) THEN RETURN
2211 IF (XAP(J - 1) > 585) OR (XAP(J - 1)  < 218) THEN RET
URN
2212 IF (YAP(J -1) > 165) OR (YAP(J -1) < -1) THEN RETURN
2220 LINE(XAP(J-1),YAP(J-1))-(XAP(J),YAP(J)),NC
2230 RETURN
2240 '
2250 '
2260 ' SUBROUTINE FOR DRAWING SQUARE
2270 '
2280 PRESET(XAP(J),YAP(J)),NC                'DISPLAYS PIXE
L OF X,Y COORDINATES
                                              ON THE SCREEN
,COLOR 1
2290 LINE (XAP(J)-4,YAP(J)-2)-(XAP(J)-4,YAP(J)+2),NC
2300 LINE (XAP(J)+4,YAP(J)-2)-(XAP(J)+4,YAP(J)+2),NC
2310 FOR PX = -4 TO 4
2320 PRESET (XAP(J)+PX,YAP(J)+2),NC
2330 PRESET (XAP(J)+PX,YAP(J)-2),NC
2340 PX = PX + 1
2350 NEXT PX
2360 IF (LN$ = "Y") OR (LN$ = "y") THEN GOSUB 2210
2370 RETURN
2380 '
2390 '
2400 ' SUBROUTINE FOR DRAWING TRIANGLE
2410 '
2420 PRESET(XAP(J),YAP(J)),NC                'DISPLAYS PIXE
L OF X,Y COORDINATES
                                              ON THE SCREEN
,COLOR 1
2430 FOR PX = -5 TO 5
2440 PRESET(XAP(J)-PX,YAP(J)+2),NC
2450 PX = PX + 1
2460 NEXT PX
2470 LINE (XAP(J)-5,YAP(J)+2)-(XAP(J),YAP(J)-3),NC
2480 LINE (XAP(J)+5,YAP(J)+2)-(XAP(J),YAP(J)-3),NC
2490 IF (LN$ = "Y") OR (LN$ = "y") THEN GOSUB 2210
2500 RETURN
```

```
2510 '
2520 TX = 1
2530 COLOR NC
2540 YF = 17 + T
2550 LOCATE YF,3 :PRINT "FILE";T;D$(T)
2560 LNS = 1
2570 ON T GOTO 2580,2590,2600,2610,2620,2630
2580 XAP(J) = 140 : YAP(J) = 140 : GOSUB 2120 :GOTO 2640
2590 XAP(J) = 140 : YAP(J) = 148 : GOSUB 2280 :GOTO 2640
2600 XAP(J) = 140 : YAP(J) = 156 : GOSUB 2420 :GOTO 2640
2610 XAP(J) = 140 : YAP(J) = 164 : GOSUB 2120 :GOTO 2640
2620 XAP(J) = 140 : YAP(J) = 172 : GOSUB 2280 :GOTO 2640
2630 XAP(J) = 140 : YAP(J) = 180 : GOSUB 2420 :GOTO 2640
2640 LNS = 0
2650 RETURN
2660 '
2670 '
2680 '
2690 COLOR 3
2700 LOCATE 23,1 : PRINT "                                        "
2710 LOCATE 23,1 : INPUT " ADD OPTIONS  Y/N ";AO$
2720 IF (AO$ = "Y") OR (AO$ = "y") GOTO 2750
2730 IF (AO$ = "N") OR (AO$ = "n") GOTO 2870
2740 GOTO 2710
2750 W = W + 1
2760 LOCATE 23,1 : PRINT "                                        "
2770 LOCATE 23,1 : INPUT " CHANGE X OR Y AXIS  X/Y";CA$
2780 IF (CA$ = "X") OR (CA$ = "x") GOTO 2830
2790 LOCATE 23,1 : PRINT "                                        "
2800 LOCATE 23,1 : INPUT "   Y AXIS NOW = ";YT$
2810 LOCATE (10 + W),17 : PRINT YT$
2820 GOTO 1810
2830 LOCATE 23,1 : PRINT "                                        "
2840 LOCATE 23,1 : INPUT "   X AXIS NOW = ";XT$
2850 LOCATE 24,(52 + (4*W)) : PRINT XT$
2860 GOTO 1810
2870 W = 0 : LOCATE 23,1 : PRINT "
     "
2880 LOCATE 23,1 : INPUT "CONTINUE  Y/N";CT$
2890 IF (CT$ = "Y") OR (CT$ = "y") GOTO 160
```

```
2900 IF (CT$ - "N") OR (CT$ - "n") GOTO 2920
2910 GOTO 2880
2920 END
2930 '
2940 '
2950 GOTO 1810
2960 '
2970 OPEN"I",#1,"\PROGRAMS\DATA\RESULTS\" + D$(T)
2980 INPUT#1,N : INPUT#1,EO : INPUT#1,VO
2990 INPUT#1,MB: INPUT#1,MS1: INPUT#1,MS2 : INPUT#1,MA
3000 INPUT#1,GA: INPUT#1,GM : INPUT#1,NI
3010 FOR J = 1 TO N : INPUT#1,VB(J) : NEXT J
3020 FOR J = 1 TO N : INPUT#1,VS1(J) : NEXT J
3030 FOR J = 1 TO N : INPUT#1,VS2(J) : NEXT J
3040 FOR J = 1 TO N : INPUT#1,VA(J) : NEXT J
3050 FOR J = 1 TO N : INPUT#1,PH(J) : NEXT J
3060 FOR J = 1 TO N : INPUT#1,CLM(J) : NEXT J
3070 FOR J = 1 TO N : INPUT#1,C3M(J) : NEXT J
3080 FOR J = 1 TO N : INPUT#1,XH(J) : NEXT J
3090 FOR J = 1 TO N : INPUT#1,XCL(J) : NEXT J
3100 FOR J = 1 TO N : INPUT#1,X3(J) : NEXT J
3110 FOR J = 1 TO N : INPUT#1,CB(J) : NEXT J
3120 FOR J = 1 TO N : INPUT#1,PHCL(J) : NEXT J
3130 FOR J = 1 TO N : INPUT#1,PHF(J) : NEXT J
3140 FOR J = 1 TO N : INPUT#1,XX(J) : NEXT J
3150 FOR J = 1 TO N : INPUT#1,II(J) : NEXT J
3160 FOR J = 1 TO N : INPUT#1,G(J) : NEXT J
3170 FOR J = 1 TO N : INPUT#1,DCL(J) : NEXT J
3180 FOR J = 1 TO N : INPUT#1,D3(J) : NEXT J
3190 FOR J = 1 TO N : INPUT#1,CL(J) : NEXT J
3200 FOR J = 1 TO N : INPUT#1,C3(J) : NEXT J
3210 CLOSE#1
3220 RETURN
3230 '   SUBROUTINE TO SPECIFY PARAMETERS
3240 '
3250 IF BT$ = "VB" THEN GOSUB 3440
3260 IF BT$ = "VS1" THEN GOSUB 3450
3270 IF BT$ = "VS2" THEN GOSUB 3460
3280 IF BT$ = "VA" THEN GOSUB 3470
3290 IF BT$ = "PH" THEN GOSUB 3480
```

```
3300 IF BT$ = "CLM" THEN GOSUB 3490
3310 IF BT$ = "C3M" THEN GOSUB 3500
3320 IF BT$ = "XH" THEN GOSUB 3510
3330 IF BT$ = "XCL" THEN GOSUB 3520
3340 IF BT$ = "XF" THEN GOSUB 3530
3350 IF BT$ = "CB" THEN GOSUB 3540
3360 IF BT$ = "PHCL" THEN GOSUB 3550
3370 IF BT$ = "PHF" THEN GOSUB 3560
3380 IF BT$ = "DCL" THEN GOSUB 3570
3390 IF BT$ = "DF" THEN GOSUB 3580
3400 IF BT$ = "PCL" THEN GOSUB 3590
3410 IF BT$ = "PF" THEN GOSUB 3600
3420 '
3430 RETURN
3440 FOR I = 1 TO N : BT(I) = VB(I) : NEXT : RETURN
3450 FOR I = 1 TO N : BT(I) = VS1(I) : NEXT : RETURN
3460 FOR I = 1 TO N : BT(I) = VS2(I) : NEXT : RETURN
3470 FOR I = 1 TO N : BT(I) = VA(I) : NEXT : RETURN
3480 FOR I = 1 TO N : BT(I) = PH(I) : NEXT : RETURN
3490 FOR I = 1 TO N : BT(I) = CLM(I) : NEXT : RETURN
3500 FOR I = 1 TO N : BT(I) = C3M(I) : NEXT : RETURN
3510 FOR I = 1 TO N : BT(I) = XH(I) : NEXT : RETURN
3520 FOR I = 1 TO N : BT(I) = XCL(I) : NEXT : RETURN
3530 FOR I = 1 TO N : BT(I) = X3(I) : NEXT : RETURN
3540 FOR I = 1 TO N : BT(I) = CB(I) : NEXT : RETURN
3550 FOR I = 1 TO N : BT(I) = PHCL(I) : NEXT : RETURN
3560 FOR I = 1 TO N : BT(I) = PHF(I) : NEXT : RETURN
3570 FOR I = 1 TO N : BT(I) = LOG(ABS(DCL(I))) / 2.302585
: NEXT : RETURN
3580 FOR I = 1 TO N : BT(I) = LOG(ABS(D3(I))) / 2.302585 :
 NEXT : RETURN
3590 FOR I = 1 TO N : BT(I) = -LOG(CL(I) * G(I)) / 2.30258
5  : NEXT : RETURN
3600 FOR I = 1 TO N : BT(I) = -LOG(C3(I) * G(I)) / 2.30258
5  : NEXT : RETURN
```

APPENDIX P4.7 NULL TEST PROGRAM

```
10 REM NULL TEST PROGRAM UPDATED 4/11/86 FILENAME ACTEST
20 CLS
30 H =40
40 DIM VB(H),VA(H),PH(H),E1(H),E2(H),E3(H),G(H),PA2(H),PA3
(H)
50 DIM CL(H),C3(H),PCL(H),PC3(H),XX(H),VS1(H),VS2(H),VS2T(
H)
60 DIM XCL(H),X3(H),XH(H),CB(H),OH(H),II(H),VX(H),GT(H),H(
H)
70 DIM CLMT(H),C3MT(H),IIT(H),HT(H),OHT(H),VBT(H),VS1T(H),
CLT(H)
80 DIM VAT(H),CLM(H),C3M(H),DCL(H),DC3(H),PHT(H),VT(H),V(H
),C3T(H)
90 PRINT: PRINT: PRINT
100 PRINT: PRINT"THE FIRST ISE RECORDED IS A HYDROGEN ELEC
TRODE"
110 PRINT"THE SECOND ISE RECORDED IS A CHLORIDE ELECTRODE"
120 PRINT"THE THIRD ISE RECORDED IS A SODIUM ELECTRODE"
130 PRINT"THE ADDED ACID, VA, IS HYDROCHLORIC ACID"
140 PRINT"THE CHLORIDE CONTAINING SALT IS RECORDED AS VS1"
150 PRINT"AND ALL SALTS ADDED ARE SODIUM SALTS."
160 PRINT: PRINT"THIS PROGRAM CALCULATES A STRAIGHT LINE F
IT"
170 PRINT"FOR ELECTRODE CALIBRATION DATA"
180 PRINT: PRINT"AND DOES NOT SCREEN PRINT RESULTS"
190 PRINT: INPUT"ENTER FILE NAME ";NM$
200 '
210 ' INPUT OF ELECTRODE CALIBRATION DATA AND RAW DATA FRO
M CREATE2 PROGRAM
220 '
230 INFILE$ = "\PROGRAMS\DATA\" + NM$
240 OPEN INFILE$ FOR INPUT AS #1
250 INPUT#1,N: INPUT#1,EO: INPUT#1,VO
260 INPUT#1,MB: INPUT#1,MS1: INPUT#1,MS2 : INPUT#1,MA
270 INPUT#1,GA: INPUT#1,GM: INPUT#1,NI
280 INPUT#1,A(1): INPUT#1,B(1): INPUT#1,A(2)
```

```
290 INPUT#1,B(2): INPUT#1,A(3): INPUT#1,B(3)
300 INPUT#1,AA(1): INPUT#1,BB(1): INPUT#1,CC(1)
310 INPUT#1,AA(2): INPUT#1,BB(2): INPUT#1,CC(2)
320 INPUT#1,AA(3): INPUT#1,BB(3): INPUT#1,CC(3)
330 FOR I = 1 TO N
340 INPUT#1,VB(I): INPUT#1,VS1(I): INPUT#1,VS2(I) : INPUT#
1,VA(I):
350 INPUT#1,E1(I): INPUT#1,E2(I): INPUT#1,E3(I)
360 NEXT
370 CLOSE #1
380 '
390 ' ACTIVITY COEFFICIENT SUBROUTINE
400 '
410 GOTO 440
420 F = EXP (-1.1513 * (SQR(F)/(1 + SQR(F)) - .3 * F )) :
RETURN
430 '
440 ' ACTIVITY CALCULATIONS FROM ISE TITRATION READINGS
450 ' CONVERTED TO CONCENTRATIONS FOR STORAGE
460 ' ALSO UPTAKE CALCULATIONS FOR ISE READINGS
470 '
480 'DISPLAYS NO. OF DATA POINT BEING PROCESSED
490 CLS
500 LOCATE 15,30 : PRINT "CALCULATIONS IN PROGRESS"
510 FOR I = 1 TO N
520 LOCATE 15,25 : PRINT I
530 '
540 ' IONIC STRENTH AND ACTIVITY COEFFICIENT CALCULATIONS
550 '
560 G(I) = 1
570 V(I) = VO + VB(I) + VS1(I) + VS2(I) +VA(I)
580 ON NI GOTO 610,600,590
590 C3(I) = EXP (-2.3026 * ( E3(I) - A(3) ) / B(3)) / G(I)
600 CL(I) = EXP (-2.3026 * ( E2(I) - A(2) ) / B(2)) / G(I)
610 H(I) = EXP (-2.3026 * ( E1(I) - A(1) ) / B(1)) / G(I)
620 OH(I) = 1E-14 / (H(I) * G(I) ^ 2)
630 II(I) = CL(I) +C3(I) +OH(I)
640 F = II(I): GOSUB 420: Y = F
650 IF G(I) / Y < 1.0001 THEN 700
660 G(I) = Y
```

```
670 GOTO 570
680 '
690 '
700 ' PC FOR EACH SALT
710 '
720 ON NI GOTO 750,740,730
730 PC3(I) = - LOG (C3(I) * G(I)) / 2.3026
740 PCL(I) = - LOG (CL(I) * G(I)) / 2.3026
750 PH(I) = - LOG (H(I) * G(I)) / 2.3026
760 '
770 '
780 ' PA FOR EACH SALT
790 '
800 PA2(I) =  PCL(I) + PH(I)
810 PA3(I) =  PC3(I) + PH(I)
820 '
830 '
840 ' MMOLES OF EACH SALT MEASURED
850 '
860 H(I) = H(I) * V(I)
870 CLM(I) = CL(I) * V(I)
880 C3M(I) = C3(I) * V(I)
890 OH(I) = OH(I) * V(I)
900 '
910 '
920 '  MMOLES OF EACH SALT ADDED
930 '
940 A = VA(I) * MA
950 B = VB(I) * MB
960 '
970 '
980 '  UPTAKE OF EACH SALT
990 '
1000  XCL(I) = (( VS1(I) * MS1 ) + CLM(1) + A   - CLM(I) )
 / GM
1010  X3(I) = ((VS1(I) * MS1) + (VS2(I) * MS2) + (VB(I) *
MB) - C3M(I)) / GM
1020 XH(I) = ( A + H(1) - B + OH(1) + OH(I) - H(I) ) / GM
1030 CB(I) = CL(I) + (OH(I)/V(I)) - (C3(I) + (H(I)/V(I)))
1040 '
```

```
1050 '
1060 ' DISTRIBUTION COEFFICIENTS
1070 '
1080 DCL(I) = XCL(I) / CL(I)
1090 DC3(I) = X3(I) / C3(I)
1100 '
1110 '
1120 '  RENAME VARIABLES IN TEST FILE
1130 '
1140 LET NT = N : LET EOT = EO : LET VOT = VO
1150 LET MS1T = MS1: LET MS2T = MS2: LET MBT = MB
1160 LET MAT = MA : LET GAT = GA
1170 LET GMT = GM: LET NIT = NI
1180 LET VBT(I) = VB(I) : LET C3MT(I) = C3M(I)
1190 LET VS1T(I) = VS1(I): LET CLMT(I) = CLM(I)
1200 LET VS2T(I) = VS2(I) : LET IIT(I) = II(I)
1210 LET VAT(I) = VA(I) : LET OHT(I) = OH(I)
1220 LET GT(I) = G(I) : LET HT(I) = H(I)
1230 LET VT(I) = V(I) : LET PHT(I) = PH(I)
1240 LET CLT(I) = CL(I) : LET C3T(I) = C3(I)
1250 NEXT
1260 '
1270 ' INPUT COMPARISON FILE DATA AND PROCESS
1280 '
1290 PRINT: INPUT"ENTER FILE NAME OF COMPARISON RUN WITH C
RYSTALS PRESENT ";N$
1300 INFILE$ = "\PROGRAMS\DATA\" + N$
1310 OPEN INFILE$ FOR INPUT AS #1
1320 INPUT#1,N: INPUT#1,EO: INPUT#1,VO
1330 INPUT#1,MB: INPUT#1,MS1: INPUT#1,MS2 : INPUT#1,MA
1340 INPUT#1,GA: INPUT#1,GM: INPUT#1,NI
1350 INPUT#1,A(1): INPUT#1,B(1): INPUT#1,A(2)
1360 INPUT#1,B(2): INPUT#1,A(3): INPUT#1,B(3)
1370 INPUT#1,AA(1): INPUT#1,BB(1): INPUT#1,CC(1)
1380 INPUT#1,AA(2): INPUT#1,BB(2): INPUT#1,CC(2)
1390 INPUT#1,AA(3): INPUT#1,BB(3): INPUT#1,CC(3)
1400 FOR I = 1 TO N
1410 INPUT#1,VB(I): INPUT#1,VS1(I): INPUT#1,VS2(I) : INPUT
#1,VA(I):
1420 INPUT#1,E1(I): INPUT#1,E2(I): INPUT#1,E3(I)
```

```
1430 NEXT
1440 CLOSE #1
1450 FOR I = 1 TO N
1460 G(I) = 1
1470 V(I) = VO + VB(I) + VS1(I) + VS2(I) + VA(I)
1480 ON NI GOTO 1510,1500,1490
1490 C3(I) = EXP (-2.3026 * ( E3(I) - A(3) ) / B(3)) / G(I
)
1500 CL(I) = EXP (-2.3026 * ( E2(I) - A(2) ) / B(2)) / G(I
)
1510 H(I) = EXP (-2.3026 * ( E1(I) - A(1) ) / B(1)) / G(I)
1520 OH(I) = 1E-14 / (H(I) * G(I) ^ 2)
1530 II(I) = CL(I) +C3(I) +OH(I)
1540 F = II(I): GOSUB 420: Y = F
1550 IF G(I) / Y < 1.0001 THEN 1590
1560 G(I) = Y
1570 GOTO 1470
1580 '
1590 '  BURET HCL CAPACITY CALCULATED CONSIDERING VOLUME E
FFECTS
1600 '  AND ACTIVITY COEFFICIENTS DIVIDED BY GRAM MATERIAL
1610 '  IN DISPERSION (COMPARISON) EXPERIMENT
1620 '
1630 VX(I) = (VBT(I) * MBT) - (VBT(1) * MBT) - (VAT(I) * M
AT)
1640 XX(I) = - ( (VB(I)*MB) - (V(I) * GT(I)) / (VT(I) *G(I
)) * VX(I) ) / GM
1650 NEXT
1660 INFILE$ = "\PROGRAMS\DATA\RESULTS\" + NM$
1670 OPEN INFILE$ FOR OUTPUT AS #1
1680 WRITE#1,NT: WRITE#1,EOT: WRITE#1,VOT
1690 WRITE#1,MBT: WRITE#1,MS1T: WRITE#1,MS2T: WRITE#1,MAT
1700 WRITE#1,GAT: WRITE#1,GMT: WRITE#1,NIT
1710 FOR I = 1 TO N: WRITE#1,VBT(I): NEXT
1720 FOR I = 1 TO N: WRITE#1,VS1T(I): NEXT
1730 FOR I = 1 TO N: WRITE#1,VS2T(I): NEXT
1740 FOR I = 1 TO N: WRITE#1,VAT(I): NEXT
1750 FOR I = 1 TO N: WRITE#1,PHT(I): NEXT
1760 FOR I = 1 TO N: WRITE#1,CLMT(I): NEXT
1770 FOR I = 1 TO N: WRITE#1,C3MT(I): NEXT
```

```
1780 FOR I = 1 TO N: WRITE#1,XH(I): NEXT
1790 FOR I = 1 TO N: WRITE#1,XCL(I): NEXT
1800 FOR I = 1 TO N: WRITE#1,X3(I): NEXT
1810 FOR I = 1 TO N: WRITE#1,CB(I): NEXT
1820 FOR I = 1 TO N: WRITE#1,PA2(I): NEXT
1830 FOR I = 1 TO N: WRITE#1,PA3(I): NEXT
1840 FOR I = 1 TO N: WRITE#1,XX(I): NEXT
1850 FOR I = 1 TO N: WRITE#1,IIT(I): NEXT
1860 FOR I = 1 TO N: WRITE#1,GT(I): NEXT
1870 FOR I = 1 TO N: WRITE#1,DCL(I): NEXT
1880 FOR I = 1 TO N: WRITE#1,DC3(I): NEXT
1890 FOR I = 1 TO N: WRITE#1,CLT(I): NEXT
1900 FOR I = 1 TO N: WRITE#1,C3T(I): NEXT
1910 CLOSE #1
1920 CLS
1930 INPUT"DO YOU WANT A HARD COPY OF THIS DATA (Y/N) ";P$
1940 IF P$ = "Y" GOTO 1960
1950 IF P$ = "N" GOTO 1970
1960 RUN "PR5"
1970 END
```

APPENDIX P4.8 SODIUM UPTAKE PROGRAM

```
10 REM SODIUM UPTAKE PROGRAM UPDATED 21/10/86 FILENAME ACT
NA
20 CLS
30 H =40
40 DIM VB(H),VA(H),E1(H),E2(H),E3(H),G(H),PA1(H),PA2(H),PA
3(H),H(H)
50 DIM C3(H),PH(H),PCL(H),PC3(H),XX(H),VS1(H),VS2(H),CLM(H
),C3M(H)
60 DIM XCL(H),X3(H),XH(H),CB(H),OH(H),II(H),CL(H),DCL(H),D
C3(H)
70 DIM A(H),B(H),AA(H),BB(H),CC(H)
80 PRINT: PRINT: PRINT
90 PRINT: PRINT"THE FIRST ISE RECORDED MUST BE A pH ELECTR
ODE"
100 PRINT"THE SECOND ISE RECORDED MUST BE A Cl ELECTRODE"
110 PRINT"THE THIRD ISE RECORDED MUST BE A Na ELECTRODE"
120 PRINT"THE ADDED ACID, VA, WILL BE HYDROCHLORIC ACID"
130 PRINT"THE CHLORIDE CONTAINING SALT IS RECORDED AS VS1"
140 PRINT"AND ALL SALTS ADDED ARE SODIUM SALTS"
150 PRINT: PRINT"THIS PROGRAM CALCULATES A STRAIGHT LINE F
IT"
160 PRINT"FOR ELECTRODE CALIBRATION DATA"
170 PRINT: INPUT"ENTER FILE NAME ";NM$
180 PRINT: INPUT "SKIP SCREEN PRINT OF RESULTS ? (Y/N) ";S
K$
190 '
200 ' INPUT OF ELECTRODE CALIBRATION DATA AND RAW DATA FRO
M CREATE2 PROGRAM
210 '
220 INFILE$ = "\PROGRAMS\DATA\" + NM$
230 OPEN INFILE$ FOR INPUT AS #1
240 INPUT#1,N: INPUT#1,EO: INPUT#1,VO
250 INPUT#1,MB: INPUT#1,MS1: INPUT#1,MS2 : INPUT#1,MA
260 INPUT#1,GA: INPUT#1,GM
270 INPUT#1,NI
280 INPUT#1,A(1): INPUT#1,B(1): INPUT#1,A(2)
```

```
290 INPUT#1,B(2): INPUT#1,A(3): INPUT#1,B(3)
300 INPUT#1,AA(1): INPUT#1,BB(1): INPUT#1,CC(1)
310 INPUT#1,AA(2): INPUT#1,BB(2): INPUT#1,CC(2)
320 INPUT#1,AA(3): INPUT#1,BB(3): INPUT#1,CC(3)
330 FOR I = 1 TO N
340 INPUT#1,VB(I): INPUT#1,VS1(I): INPUT#1,VS2(I) : INPUT#
1,VA(I):
350 INPUT#1,E1(I): INPUT#1,E2(I): INPUT#1,E3(I)
360 NEXT
370 CLOSE #1
380 PRINT
390 '
400 ' ACTIVITY COEFFICIENT SUBROUTINE
410 '
420 GOTO 440
430 F = EXP (-1.1513 * (SQR(F)/(1 + SQR(F)) - .3 * F )) :
RETURN
440 '
450 '
460 ' ACTIVITY CALCULATIONS FROM ISE TITRATION READINGS
470 ' CONVERTED TO CONCENTRATIONS FOR STORAGE
480 ' ALSO UPTAKE CALCULATIONS FROM ISE READINGS
490 '
500 CLS
510 LOCATE 15,30 : PRINT "CALCULATIONS IN PROGRESS"
520 FOR I = 1 TO N
530 '
540 '
550 'DISPLAYS NO. OF DATA POINT BEING PROCESSED
560 '
570 IF (SK$ = "Y") OR (SK$ = "y") GOTO 590
580 GOTO 640
590 LOCATE 15,25 : PRINT I
600 '
610 '
620 ' IONIC STRENTH AND ACTIVITY COEFFICIENT CALCULATIONS
630 '
640 G(I) = 1
650 V = VO + VB(I) + VS1(I) + VS2(I) +VA(I)
660 ON NI GOTO 690,680,670
```

```
670 C3(I) = EXP (-2.3026 * ( E3(I) - A(3) ) / B(3)) / G(I)
680 CL(I) = EXP (-2.3026 * ( E2(I) - A(2) ) / B(2)) / G(I)
690 H(I) = EXP (-2.3026 * ( E1(I) - A(1) ) / B(1)) / G(I)
700 OH(I) = 1E-14 / (H(I) * G(I) ^ 2)
710 II(I) = CL(I) +C3(I) +OH(I)
720 F = II(I): GOSUB 430: Y = F
730 IF G(I) / Y < 1.0001 THEN 780
740 G(I) = Y
750 GOTO 650
760 '
770 '
780 ' PC FOR EACH SALT
790 '
800 ON NI GOTO 830,820,810
810 PC3(I) = - LOG (C3(I) * G(I)) / 2.3026
820 PCL(I) = - LOG (CL(I) * G(I)) / 2.3026
830 PH(I) = - LOG (H(I) * G(I)) / 2.3026
840 '
850 '
860 ' PA FOR EACH SALT
870 '
880 PA2(I) =  PCL(I) + PH(I)
890 PA3(I) =  PC3(I) + PH(I)
900 '
910 '
920 ' MMOLES OF EACH SALT MEASURED
930 '
940 H(I) = H(I) * V
950 CLM(I) = CL(I) * V
960 C3M(I) = C3(I) * V
970 OH(I) = OH(I) * V
980 '
990 '
1000 '  MMOLES OF EACH SALT ADDED
1010 '
1020 A = VA(I) * MA
1030 B = VB(I) * MB
1040 '
1050 '
1060 '  UPTAKE OF EACH SALT
```

```
1070 '
1080  XCL(I) = (( VS1(I) * MS1 ) + CLM(1) + A   - CLM(I) )
 / GM
1090  X3(I) = ((VS1(I) * MS1) + (VS2(I) * MS2) + (VB(I) *
MB) - C3M(I)) / GM
1100 XH(I) = ( A + H(1) - B + OH(1) + OH(I) - H(I) ) / GM
1110 CB(I) = ( CL(I) + OH(I) - C3(I) - H(I) )
1120 XX(I) = (  XCL(I) + X3(I)  )
1130 '
1140 '
1150 ' DISTRIBUTION COEFFICIENTS
1160 '
1170 DCL(I) = XCL(I) / CL(I)
1180 DC3(I) = X3(I)  / C3(I)
1190 '
1200 '
1210 ' SCREEN PRINT OF DATA DURING CALCULATIONS
1220 '
1230 IF (SK$ = "Y") OR (SK$ = "y") GOTO 1460
1240 PRINT: PRINT: PRINT
1250 PRINT " N = ";I : PRINT
1260 PRINT " PH = "; PH(I)
1270 PRINT "ACTIVITY COEFFICIENT = ";G(I)
1280 PRINT "IONIC STRENGTH = ";II(I)
1290 PRINT "MMOLES CHLORIDE = ";CLM(I)
1300 PRINT "MMOLES ISE NO.3 = ";C3M(I)
1310 PRINT "MMOLES H        = ";H(I)
1320 PRINT "MMOLES OH       = ";OH(I)
1330 PRINT "MMOLES A        = ";A
1340 PRINT "MMOLES B        = ";B
1350 PRINT "PCL             = ";PCL(I)
1360 PRINT "PA2             = ";PA2(I)
1370 PRINT "PC3             = ";PC3(I)
1380 PRINT "PA3             = ";PA3(I)
1390 PRINT "UPTAKE CHLORIDE =";XCL(I)
1400 PRINT "UPTAKE ION NO.3 =";X3(I)
1410 PRINT "UPTAKE H        = ";XH(I)
1420 PRINT "ANION BALANCE   =";XX(I)
1430 PRINT "CHARGE BALANCE  =";CB(I)
1440 PRINT "CL DIST. COEFF. =";DCL(I)
```

```
1450 PRINT "C3 DIST. COEFF. -";DC3(I)
1460 NEXT
1470 PRINT
1480 '
1490 ' OUTPUT DATA AS RESULTS FILE
1500 '
1510 INFILE$ = "\PROGRAMS\DATA\RESULTS\" + NM$
1520 OPEN INFILE$ FOR OUTPUT AS #1
1530 WRITE#1,N: WRITE#1,EO: WRITE#1,VO
1540 WRITE#1,MB: WRITE#1,MS1: WRITE#1,MS2: WRITE#1,MA
1550 WRITE#1,GA: WRITE#1,GM: WRITE#1,NI
1560 FOR I = 1 TO N: WRITE#1,VB(I): NEXT
1570 FOR I = 1 TO N: WRITE#1,VS1(I): NEXT
1580 FOR I = 1 TO N: WRITE#1,VS2(I): NEXT
1590 FOR I = 1 TO N: WRITE#1,VA(I): NEXT
1600 FOR I = 1 TO N: WRITE#1,PH(I): NEXT
1610 FOR I = 1 TO N: WRITE#1,CLM(I): NEXT
1620 FOR I = 1 TO N: WRITE#1,C3M(I): NEXT
1630 FOR I = 1 TO N: WRITE#1,XH(I): NEXT
1640 FOR I = 1 TO N: WRITE#1,XCL(I): NEXT
1650 FOR I = 1 TO N: WRITE#1,X3(I): NEXT
1660 FOR I = 1 TO N: WRITE#1,CB(I): NEXT
1670 FOR I = 1 TO N: WRITE#1,PA2(I): NEXT
1680 FOR I = 1 TO N: WRITE#1,PA3(I): NEXT
1690 FOR I = 1 TO N: WRITE#1,XX(I): NEXT
1700 FOR I = 1 TO N: WRITE#1,II(I): NEXT
1710 FOR I = 1 TO N: WRITE#1,G(I): NEXT
1720 FOR I = 1 TO N: WRITE#1,DCL(I): NEXT
1730 FOR I = 1 TO N: WRITE#1,DC3(I): NEXT
1740 FOR I = 1 TO N: WRITE#1,CL(I): NEXT
1750 FOR I = 1 TO N: WRITE#1,C3(I): NEXT
1760 CLOSE #1
1770 CLS
1780 INPUT"DO YOU WANT A HARD COPY OF THIS DATA (Y/N) ";P$
1790 IF P$ = "Y" GOTO 1810
1800 IF P$ = "N" GOTO 1820
1810 RUN "PR5"
1820 END
```

LIST OF SYMBOLS

Symbol	Name
A	Constant, defined by Debye-Hückel; 0.51
A_o	Constant, linear eq. of least squares
A_1	Slope, linear eq. of least squares
a	Effective diameter of a single hydrated ion
a_i'	Activity of ion, i, on one side of membrane
a_i''	Activity of ion, i, other side of membrane
a_{H^+}	Activity of hydrogen ion
AT	mmoles acid added in control
B	Constant, defined by Debye-Hückel; 0.328
B	mmoles base in uptake calculations
B_o	Constant, curve fit of least squares
B_1	Slope, curve fit of least squares
B_2	Curvature, curve fit of least squares
BT	mmoles base added in control
BT_i	mmoles base to get to starting pH in control
c_i	Concentration of ion, i
C3M	mmoles sodium read by sodium ISE
D_i	Distribution coefficient for ion, i
E	Electric potential, emf, of a half cell
E_{cell}	Electric potential, emf, of a cell
E_o	Constant term in the Nernst equation
F	Faraday constant
G	Grams of oxide hydroxide
I	Ionic strength

LIST OF SYMBOLS, continued

Symbol	Name
K_a	Acid dissociation constant
K_b	Base dissociation constant
M	Molarity of solution
pA	- log of total acid activity
pB	- log of total base activity
pH	- log of hydrogen ion activity
pX	- log of ion, X, activity
R	Gas constant
S1	mmoles salt 1 in uptake calculations
S2	mmoles salt 2 in uptake calculations
T	Absolute temperature
V	Total volume, ml
V_o	Initial volume, ml
V_a	Volume of acid, ml
V_b	Volume of base, ml
V_{s1}	Volume of salt 1, ml
V_{s2}	Volume of salt 2, ml
VT	Total volume in control, ml
X	Absolute capacity, mmol/g
X_o	Initial capacity (also denoted as ΔX_{max})
ΔX	Change in capacity
XCl	Capacity, mmol/g, for chloride ion
XNa	Capacity, mmol/g, for sodium ion
XX	Capacity, mmol/g, from HCl burette in control
z_i	Charge of ion, i

Greek Letters

α	Alpha, denotes geothite in iron oxides
β	Beta, denotes akaganeite in iron oxides
γ_i	Activity coefficient of ion, i
γT	Activity coefficient in control
$\bar{\psi}-\psi$	Donnan potential